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Et
SPECTRUM ANALYSIS.

BY

JOHN LANDAUER, LL.D.,

Member of the Imperial German Academy of Naturalists.

AUTHORIZED ENGLISH EDITION

BY

J. BISHOP TINGLE, PH.D., F.C.S.,

*Instructor of Chemistry in the Lewis Institute,
Chicago, Ill.*

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AUTHOR'S PREFACE.

THIS work originated as a reprint of an article on Spectrum Analysis recently contributed to Fehling-Hell's "Neues Handwörterbuch der Chemie"; it was published as a separate book at the request of a number of competent authorities, but not without some hesitation on the part of the author, because in treating a subject in an encyclopedic article regard must be paid to the whole plan and scope of the work, whilst in a separate book the author is quite independent.

The favorable reception accorded to the book when published gives rise to the hope that shortcomings arising from its origin are to some extent counterbalanced by a fulness of contents brought together in small space, by the strictly historical treatment of the subject adopted throughout the book, by tolerably full bibliographical references, and by the care which has been bestowed on the numerical tables serving for reference. In order to secure a degree of uniformity hitherto wanting, the older measurements have been recalculated so as to bring them into accord with Rowland's system of wave-lengths.

THE AUTHOR.

BRAUNSCHWEIG, 1898.

ABBREVIATIONS.

THE following abbreviations have been used in the bibliographical references:

- A. B. A. = Abhandlungen der Königlichen Akademie der Wissenschaften zu Berlin.
- A. c. p. = Annales de chimie et de physique.
- B. A. R. = British Association Reports.
- C. N. = Chemical News.
- C. r. = Comptes rendus hebdomadaires des Séances de l'Académie de Sciences, Paris.
- N. = Nature.
- N. A. S. U = Nova Acta Regiæ Societatis Scientiarum Upsaliensis.
- P. A. = Poggendorff's Annalen der Physik und Chemie.
- P. M. = Philosophical Magazine.
- P. M. P. S. = Proceedings of the Manchester Literary and Philosophical Society.
- P. R. S. = Proceedings of the Royal Society.
- P. R. S. E. = Proceedings of the Royal Society, Edinburgh.
- P. T. = Philosophical Transactions.
- P. T. E. = Philosophical Transactions, Edinburgh.
- T. R. S. E. = Transactions of the Royal Society, Edinburgh.
- W. A. = Wiedemann's Annalen der Physik und Chemie.

TRANSLATOR'S PREFACE.

THE claim of spectrum analysis to a place in a chemical curriculum is steadily obtaining increased recognition, and its importance is generally admitted both for students preparing for teaching, and for those who wish to engage in technological work. The subject may rightly demand a wider field since its pursuit furnishes so many opportunities for an excellent training in accuracy of observation and manipulative skill that it might, with great advantage, find place in a general science course. The expense is by no means prohibitive, and is almost entirely confined to the first cost of the instruments, which, with proper care, last for years, and even with the cheaper and smaller ones, such as Browning's "Students' Spectroscope," which costs about \$30, much interesting work can be done and valuable discipline obtained.

Of the works on spectrum analysis hitherto published in English, none are suitable as text-books, either on account of their size and consequent cost, or from the manner in which the subject is presented.

It is hoped that this little book may, in some degree, supply this lack.

There has been no attempt to treat the subject exhaustively, but rather to indicate the more salient points of theory, etc., leaving it to the teacher to complete and expand them at his own discretion.

No doubt it would be well if all students were compelled to take a course in general physics before attacking chemistry,

but at present this is a state of things not realized in practice; to those who have followed such a course the physical section of the book should be superfluous; but it may serve to call the attention of the others to matters on which they should obtain more instruction. The tables of wave-lengths will, it is hoped, be useful in the practical work which would probably constitute the greater portion of the course. The position of the more prominent lines and bands can, by their help, be at once ascertained, and their actual occurrence and identification facilitated.

LEWIS INSTITUTE,
CHICAGO, ILL., Dec. 1897.

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SPECTRUM ANALYSIS.

CHAPTER I.

INTRODUCTORY. HISTORICAL.

SPECTRUM ANALYSIS is a chemico-analytical method by means of which it is possible to determine the constituents of a substance, by observing the refraction (dispersion), or the diffraction of light-rays. Its further development offers a means of investigating the molecular structure of matter. The image which is produced when light-rays are refracted is termed a spectrum. White-hot solid bodies emit rays of all refrangibility, and give a *continuous* spectrum; glowing gases or vapors emit rays of definite refrangibility, and therefore yield a *discontinuous* spectrum consisting of bright lines which are characteristic of each substance, and which consequently serve for its identification whether it occurs alone, or together with other bodies. When the rays from a white-hot solid pass through a colored medium some of them are retained giving an *absorption spectrum*, which varies with the chemical composition of the medium.

Spectra-reactions are characterized by an extreme delicacy far exceeding that of chemical tests, and therefore their employment has led to the discovery of a number of new elements which occur only in small quantity. Since the distance of the source of light has little effect on a spectrum, the method can be employed for the investigation of celestial

bodies: it has extended our knowledge of their nature to an extent which was previously entirely unattainable.

Historical.¹—Spectrum Analysis was founded by Kirchhoff and Bunsen in 1859, and subsequently developed. Other observers had previously noticed spectrum lines, and had suggested the application of spectroscopic observations to chemical analysis, but their efforts were fruitless, as at that time it was not certain whether the bright lines of a glowing gas were solely dependent on its chemical composition. The sodium reaction was particularly misleading as it was often observed when the presence of this metal was not suspected, and was therefore variously ascribed to sodium, to sulphur, or to water. The yellow sodium flame was first noticed by Thomas Melville² in 1752, but he was unable to determine its origin. John Herschel³ in 1822 investigated the spectra of many colored flames, particularly those given by strontium, copper, and boric acid, and in 1827 showed that by this means the substances giving the colors could be recognized even when present only in extremely small quantity. Fox Talbot⁴ in 1826 expressed himself still more definitely, stating that if his theory that certain bodies gave characteristic lines should prove to be correct, then a glance at the prismatic spectrum of a flame would suffice to identify substances which would otherwise require a tedious chemical analysis for their detection. In 1834 he correctly described the lithium and strontium spectra, and again pointed out that

¹ Kopp, *Entwicklung der Chemie in der neuen Zeit* (München, 1873), pp. 215, 642. Kirchhoff, *Zur Geschichte der Spectralanalyse*. P. A. 118, 94, 102. Brewster, C. r. 62, 17. Kahlbaum, *Aus der Vorgeschichte der Spectralanalyse* (Basel, 1888). Rosenberger, *Geschichte der Physik*, 3 (Braunschweig, 1890). Stokes, N. 13, 188. P. M. [4] 25, 250. Talbot, P. R. S. E. 7, 461.

² Edinb. Phys. and Lit. Essays, 2, 12.

³ T. R. S. E. (1823) 9. P. A. (1829) 16. On the theory of light (London, 1828).

⁴ Brewster's Journ. of Sci. 5. P. M. (1833) [3] 3, 35; (1836), 9, 3.

such optical methods permitted of the identification of these elements with a minimum quantity of substance, and with an exactitude equalling, if not excelling, that attained by any other process. Doubt was, however, cast on this conclusion by contradictory statements in the same communications, and the method of analysis was rendered fundamentally dubious, because, in opposition to Herschel, Talbot maintained that the reactions could be produced by the simple presence of the substance in the flame, its volatilization not being necessary. W. A. Miller¹ published in 1845 an investigation on the spectra of the alkali metals; diagrams were given, but the results did not constitute any great advance, as he had employed a luminous flame, and was therefore unable to determine what was characteristic of any particular metal. In 1856 Swan² definitely proved that the yellow line which is almost always present is peculiar to sodium compounds, and that the frequency of its occurrence is due to the almost universal distribution of sodium salts. In his work on the prismatic spectra of the hydrocarbons Swan showed that the lines observed are constant in position; he thus made a valuable contribution towards the solution of the question as to whether the bright lines of a glowing gas are exclusively dependent on its chemical composition. The definite and general answer to this problem was, however, not given by Swan, but by Kirchhoff and Bunsen.

The spectra of the electric spark had been under observation simultaneously with those of flames; Wollaston³ detected a large number of bright lines, but without offering any clue to their origin. He was also the first to describe the dark lines in the solar spectrum, and he improved the apparatus employed by substituting a narrow slit for the circular opening which Newton had used to admit the light.

¹ B. A. R. 1845. P. M. [3] 27, 81.

² T. R. S. E. 3, 376; (1857) 21, 353.

³ P. T. 1802. p. 365.

Fraunhofer¹ was scarcely more successful than Wollaston so far as the origin of the bright lines was concerned; his fame rests on the discovery of the diffraction grating, the measurement of wave-lengths which its use permitted, and on the observation of the dark lines in the solar spectrum which bear his name. He drew 350 of these, and finding that they varied from those observed in stellar spectra, he concluded that they originate in the sun and stars, and are not due to the earth's atmosphere. Wheatstone² in 1835 found that with the use of different metallic electrodes the spectra vary, but they remain constant no matter whether the discharge takes place in air, hydrogen, or in a vacuum; he therefore concluded that the metal is volatilized, but not burnt, by the passage of the spark. He published drawings of the spectra of sodium, mercury, zinc, cadmium, bismuth, tin, and lead, and recommended the method for analytical purposes.

The spectra of various metals volatilized in air were studied, although less thoroughly, by Foucault³ in 1849; he also observed the dark *D*-line, since known as the reversed sodium line, but failed to draw the important conclusion from this which Kirchhoff subsequently made. Masson,⁴ who improved the method of working, using condensers charged by induction-currents, investigated the spark-spectra of iron, tin, antimony, bismuth, copper, lead, cadmium, and carbon; in all these cases he noticed that the lines due to moist air were present, although he was ignorant of their origin. This was indicated by Ångström's⁵ important work published in 1853. He showed that the lines which occur in the space between the electrodes are due to air or to any other gas

¹ Denkschriften der Münchener Akad., 1814, 1815; Gilbert's Ann. 74, 337.

² B. A. R. 1835. C. N. 3, 198. P. M. [3] 7.

³ Institut. 1849, p. 44.

⁴ A. c. p. (1851) [3] 31, 295.

⁵ K. Vetenskaps Akad. Handl. (Stockholm, 1853), p. 335. P. A. (1855) 94, 141.

which may be present, whilst those close to the electrodes are given by the metals. Ångström also drew and described the spectra of a large number of metals and non-metals, and almost discovered the relationship between the emission and absorption of light, since he stated, in accordance with a suggestion of Euler, that at a common temperature bodies absorb the same vibrations which they are capable of producing. In 1858 Plücker¹ commenced his investigations of the spectra produced by the passage of an electric current through highly rarefied gases. He found that the elementary gases, or the constituents liberated from compound gases, are characterized by bright lines. Similar work was pursued by van der Willigen,² who in 1859 also showed that platinum electrodes moistened with a salt solution give the spectrum of the salt, and that it is therefore unnecessary to use the metal itself in order to obtain its spectrum. In the same year Kirchhoff and Bunsen³ published their work "*Chemische Analyse durch Spectralbeobachtungen*"; their results were obtained to some extent independently of previous investigators who, whilst frequently on the right path, had failed to reach the goal. They reduced spectral phenomena to a chemical-analytical method, and definitely proved that the bright lines produced by a glowing gas are dependent only on its chemical composition. This law still forms the basis of spectrum analysis, but their second proposition has been subsequently considerably modified; it states that the manner in which the constituents of a substance are combined is without influence on their spectra, and that these are also almost entirely unaffected by the temperature and pressure of the vapor. After Roscoe and Clifton⁴ had called attention to the difference between the spectrum of an element and those of its compounds, A. Mitscherlich⁵ showed, in 1863, that every

¹ P. A. 103, 88; 104, 113, 622; 105, 67; 107, 77, 415.

² P. A. 106, 610; (1859) 107, 473. ³ P. A. 110, 167.

⁴ P. M. P. S. 1862.

⁵ P. A. (1863) 121, 3.

compound has its own peculiar spectrum, and that the exhibition of identical spectra by the various salts of an element is caused by these undergoing dissociation. In their first communication Kirchhoff and Bunsen described the spectra of the metals of the alkalis and alkaline earths, and showed the great delicacy of the method, which permits of the recognition of substances when present in quantity far too small for detection by the ordinary processes; they also pointed out the great extension which it gives to our knowledge of the distribution of the elements, and indicated that it would probably lead to the recognition of new ones. The correctness of this view has been proved by the discovery of cæsium, rubidium, thallium, indium, gallium, and many metals of the rare earths, all by means of spectrum analysis.

The development of spectrum analysis received a special impulse from its application to astronomy. Kirchhoff¹ proved mathematically that for every ray of light the relationship between the emissive and absorptive powers of all bodies is alike at uniform temperatures; this explained the origin of the Fraunhofer lines, and led to the investigation of the chemical composition of the sun and its atmosphere. The discovery of this law of exchanges induced Kirchhoff to prepare more exact drawings of the solar spectrum, and to accurately compare the positions of the Fraunhofer lines with those in the spectra of many terrestrial substances. He employed for this purpose an arbitrary scale, as did also Huggins,² who extended these observations. To Ångström³ belongs the credit of substituting the wave-length for the scale as a means of determining the position of the lines, and his measurements, and atlas of the solar lines, remained for twenty years the foundation of all spectroscopic investigations. Ångström's work was

¹ Monatsber. Berl. Akad., Oct. 27, 1859.

² P. T. (1864) 154.

³ Recherches sur le spectre normal du soleil avec atlas de 6 planches. Upsala, 1868.

confined to the visible portion of the spectrum; it was completed by Cornu's¹ researches on the ultra-violet, and by Langley's² and Abney's³ on the infra-red. After Ångström's death, Thalén⁴ showed that the metre he had employed was incorrect, and that consequently his wave-length determinations were too small. This was confirmed by Müller and Kempf⁵ in 1886; their measurements of 300 solar lines were carried out with great care, and became the basis of the Potsdam system. All these determinations were, however, exceeded in accuracy by Rowland's⁶ Atlas of the solar spectrum, and his reproductions of normal lines, published in 1888 and 1893 respectively. His discovery of the concave grating in 1891, and his "coincidence" method of determining the relative position of lines, has greatly aided spectroscopic work, since it admits of the production of photographs without the use of a lens, thus insuring a high degree of comparative accuracy.

For a considerable time the measurement of the spectra of terrestrial substances did not keep pace with that of the solar spectrum; Kirchhoff's and Huggins' determinations were duly superseded by the more accurate ones of Thalén,⁷ but these were confined to the visible spectrum. Apart from W. A. Miller's⁸ incomplete work on the ultra-violet in 1862, Lockyer⁹ in 1881 was the first to accurately investigate the

¹ Spectre normal du soleil. Partie ultraviolette (Paris, 1881), p. 22.

² P. M. [5] 21, 394; 22, 149; 26, 505.

³ P. T. 1880, p. 653. W. A. Beibl. 4, 375; 5, 507. C. r. 90, 182.

⁴ Spectre du fer. Acta R. Soc. Scient. Upsala, (1884) [3], p. 49. W. A. Beibl. 9, 520.

⁵ Publ. d. Astrophys. Obs. zu Potsdam (1886), 5.

⁶ Photographic Map of the normal Solar Spectrum, Johns Hopkins Univ., Baltimore. Astronomy and Astrophysics (1893), 12, 321. P. M. (1894) [5] 36, 49.

⁷ N. A. S. U. (1868) [3] 6.

⁸ P. T. (1862) 152, 861.

⁹ P. T. (1873) 163, 253, 639; (1874) 164, 479, 805. P. R. S. 25, 546; 27, 49, 279, 409; 28, 157.

subject, but he soon quitted it, and its fuller examination was reserved for Hartley and Adeney,¹ and Liveing and Dewar.²

Since 1888 Kayser and Runge³ have met with great success in their important task of measuring the emission-spectra of terrestrial substances by Rowland's method. They commenced the work in order to determine the relationship of the various lines of an element, and also that of the lines of different elements. Attempts had been made in this direction shortly after the discovery of spectrum analysis by Kirchhoff and Bunsen; it was at first believed that the relationship of the lines was similar to the sound-waves of a vibrating string, which consist of a fundamental note and harmonic overtones. This view was shown by Schuster⁴ in 1880 to be incorrect, and in 1885 Balmer⁵ discovered a formula which accurately reproduces the hydrogen lines in wave-lengths. These investigations, together with the observations of Liveing and Dewar⁶ on harmonic series of similar lines, are naturally connected with Kayser and Runge's work, which has led to the discovery of the methodical structure of a series of spectra. Rydberg,⁷ working independently of Kayser and Runge, has obtained similar results. Investigations of this nature have tended to greatly widen the domain of spectrum analysis.

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¹ P. T. 1884, p. 63.

² P. T. 174, 187. P. R. S. 34, 119, 123. W. A. Beibl. 6, 934; 7, 849.

³ A. B. A. 1888-1894. Runge B. A. R. 1888, 576.

⁴ B. A. R. 1880.

⁵ W. A. (1885) 25.

⁶ P. T. (1883) 174, 208.

⁷ C. r. (1890) 110, 394. K. Vetenskaps Akad. Handl., 23 (Stockholm, 1890).

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CHAPTER II.

PHYSICAL PROPERTIES OF LIGHT.¹

ACCORDING to Huygens' universally accepted theory, light consists of wave-motions of the ether, the vibrations being transmitted from particle to particle with an extremely high velocity in straight lines; the vibrations of the particles of ether are at right angles to the path of the ray. On account of the great elasticity of the ether, and the ease with which the vibrations are further propagated, single rays cannot be obtained, but only pencils consisting of a number of rays, which may be considered to be parallel if it is assumed that the vibrations are very small, or at a great distance from the source. The varying frequency of the vibrations produces in the eye the effect of color; the number of vibrations is constant for each color, but in a given medium the wave-length differs. Since all light-rays are transmitted with a uniform velocity in the free ether or in a vacuum, and almost so in air, the number of vibrations is small or great in proportion as the waves are long or short.

Wave-length.—It is possible to directly determine the wave-length corresponding with a given color in air, and it is found that at the extremity of the visible red the wave-length (λ) of the *A*-line = 0.00076 mm., that of the yellow *D*₁-line = 0.000589 mm., and that of the *K*-line at the limit of the visible violet = 0.00039 mm. The velocity (v) of light is

¹ Comp. Fehling-Hell's Handwörterbuch, 4, 87, and text-books of Physics.

known to be about 300,000 kilometres per second; the number of vibrations (n) is obtained by the expression $n = \frac{v}{\lambda}$.

In this manner it is found that the number of vibrations of the above three lines = 395, 509, and 763 billions per second respectively. These numbers are inconceivably great, and awkward to write, and it is therefore usual to define the color by the wave-length, although this varies with the medium. In dealing with wave-lengths measured in a vacuum, the millionth part of a millimetre = 0.001 mikron is taken as the unit, and, in accordance with Kayser's suggestion, it is represented by the symbol $\mu\mu$; a tenth part of this = $0.1\mu\mu$ is termed an Ångström's unit.

Reflection.—The light which falls on a rough nonluminous body is partly absorbed or transmitted and the remainder thrown back on all sides, thus making the object visible; but smooth polished surfaces—mirrors—only reflect the light in certain definite directions; the perpendicular produced at the point of the reflecting surface where the ray impinges is in the same plane as the incident and reflected ray, and both form identical angles with it.

Refraction.—The passage of light from one medium to another—for instance, from air into water or glass—causes a part of it to be thrown back in accordance with the law of reflection, whilst the remainder traverses the new medium, but

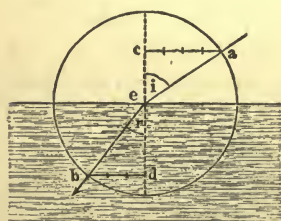


FIG. 1.

not in a straight line; its path is deflected (Fig. 1), a process which is known as refraction. The incident ray ac and the refracted ray eb are in the same plane as the normal ed of the new medium; if the light passes from a rare to a denser medium, the refracted ray approaches the perpendicular, otherwise it recedes from it. In order that refraction may take place the incident ray must form an acute angle

with the normal; if it forms a right angle, it traverses the medium in a straight line. Every incident angle corresponds with a particular refractive angle; the sine ac of the incident angle i bears a definite relationship n to the sine bd of the angle of refraction r , in accordance with Snell's law, so that

$$n = \frac{\sin i}{\sin r} \text{ or } \sin r = \frac{\sin i}{n} \text{ or } \sin i = n \sin r.$$

This relationship is termed the refractive index, or coefficient of refraction, and differs for every transparent substance. The refractive indices of the following substances are for D -light, and at a temperature of 20° :

Water	1.3333
Alcohol.....	1.3616
Carbon bisulphide.....	1.6276
α -Bromonaphthalene.....	1.6582
Ethylic cinnamate (at 18.8°).....	1.5607
Crown glass.....	1.515–1.615
Flint glass	1.614–1.762
Jena, heaviest silicate flint glass, No. 557.....	1.9625
Quartz (ordinary ray).....	1.5442
Fluor-spar	1.4339
Air (0° and 760 mm.).....	1.0002922

Plates with plane parallel surfaces cause the incident ray to be as much deflected towards the perpendicular as the issuing ray is bent from it; the two rays are therefore parallel to one another.

Prisms.—A prism is a wedge-shaped transparent object with two polished surfaces forming an angle with one another. The section of an ordinary simple glass prism forms an equilateral triangle (Fig. 2); the polished sides AB and AC are the refracting surfaces, enclosing the refracting angle a and

forming the refracting edge A . If a ray of light in the plane of the section falls on one of the sides AB or AC , it is bent at its entrance and exit, in accordance with the law of refraction, and approaches the thick portion of the prism. The extent of this deflection is equal to the angle d which the incident and issuing rays form with one

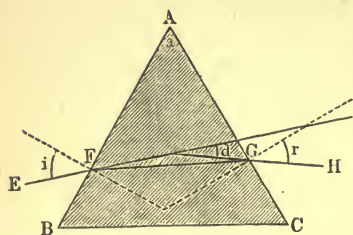


FIG. 2.

another, and is also equal to the sum of the angle of incidence and that of the issuing ray, minus the refractive angle. The angles i , r , and a bear a certain interrelationship, and it is possible to calculate in what position of the prism the refraction will be smallest; this can be confirmed by direct observation. This *minimum deviation* occurs when the ray forms the same angle with the refracting surfaces externally and internally, or, in other words, when it traverses the prism symmetrically. The refractive index n of the material of which the prism is composed may be calculated by the expression

$$n = \frac{\sin \frac{1}{2}(d + a)}{\sin \frac{1}{2}a},$$

the minimum deviation and angle of refraction being measured by means of the goniometer.

Dispersion.—Refraction not only changes the direction of a ray of light, but, if it is not homogeneous, its nature is also modified; a ray of white light is converted into a rainbow-colored band, as may be easily seen by the help of a prism. The polychromatic rays composing white light are transmitted with uniform velocity in a vacuum, but in a denser medium the more rapidly vibrating violet rays undergo a greater retardation than the red rays, which vibrate more slowly; the former are therefore refracted more strongly than

the latter. The component rays are more strongly refracted by passage through a second prism, but do not undergo any further decomposition; they are therefore simple or homogeneous, and if combined by means of a lens white light is reproduced.

These experiments, which are of fundamental importance both for spectrum analysis and for the theory of light, were first performed by Newton in 1668, and described in his "Opticks" in 1675. He allowed a ray of sunlight to pass through a small hole in a window-shutter into a darkened

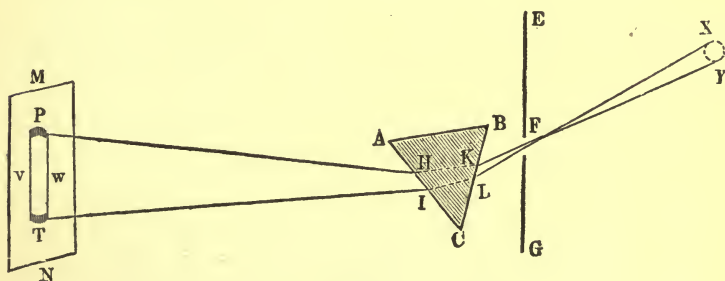


FIG. 3.

room XY (Fig. 3); he passed the rays through a prism ABC , which caused them to be deflected and resolved into the colored band PT , which he termed a spectrum, and which was received on the white screen MN . The colored rays when viewed by Newton through a second prism gave the impression of white light, but when they were made to traverse it separately they were not further decomposed, but only underwent a second refraction.

Abnormal Dispersion.—The refractive index of a medium is, as a rule, greater the smaller the wave-length of the particular light; in the visible spectrum the index steadily increases in passing from red to blue. Certain substances do not conform to this rule, their solutions, when employed as refracting and dispersing agents, exhibit the inverse relation-

ship between refractive index and dispersion. This phenomenon is termed abnormal dispersion.¹

Pure Spectra.—The colors obtained if the light is admitted to the prism through a round opening, as in Newton's experiment, are never completely separated from one another, as the circular shape of the images causes them to overlap. In order to separate the various colors as completely as possible, and obtain a pure spectrum, a narrow longitudinal slit has, since Wollaston's² time, been generally employed for the admission of the light. The number of images of the slit produced is equal to that of the different wave-lengths in the light employed, and consequently the narrower the slit the less do the images superpose; the spectrum thus obtained may be magnified to any desired extent. The resolving power of a prism, or system of prisms, is partly dependent on its dispersion, but to a greater extent, as Rayleigh³ has shown, on the distance which the ray traverses in its route through them. The thickness of heavy flint glass required to separate the *D*-lines = 1.02 cm.; taking this value, roughly 1 cm., as unit, the resolving power of a prism of similar glass in the region of the *D*-line is equal to its thickness in centimetres; in other parts of the spectrum it is inversely proportional to the cube of the wave-length, so that it is eight times greater in the violet than in the red, and therefore corresponds with the total thickness, or with the length of the base of the prism or system, but is independent of the number of prisms, of their angle, or of the order in which the various members of the system are arranged.

Gratings.—An optical grating consists of a plate with a large number of parallel lines ruled upon it; this arrangement,

¹ Christiansen, P. A. (1870) 141, 479; (1871) 143, 250. Kundt, P. A. (1871) 143, 259; 144, 128; (1872) 145, 67. Sieben, W. A. (1879) 8, 137. Sellmeier, P. A. 145, 396, 520; 147, 386, 525. H. v. Helmholtz, Monatsber. Berl. Akad. (1874), p. 667. P. A. (1874) 154, 582.

² P. T. (1802) p. 378.

³ P. M. (1879) [5] 9, 269.

like a prism, produces spectra. Gratings were first employed by Fraunhofer,¹ who at first used a wire grating prepared by winding thin wire over two similar screws of very fine thread, placed parallel to one another; later he engraved numerous fine lines, closely adjacent and at regular intervals, on gold-leaf backed by glass, and finally employed glass plates with opaque lines cut by means of a diamond. The preparation of gratings has been greatly improved in more recent times by the use of good dividing-machines. Two kinds of gratings are made, the *transparent* ones of glass, with as many as 800 lines per mm., and *reflection* gratings of speculum metal which reflects instead of transmitting the light; the latter are preferable for spectroscopic work, as less light is absorbed. Rutherford, in the United States, considerably improved the construction of the reflection grating, and since 1882 their preparation has been carried to an extraordinarily high degree of perfection by Rowland at Baltimore. His plane and concave gratings with 10,000, 14,438, and 20,000 lines per inch are almost faultless, and comparatively free from scratches caused by irregularity of the diamond-point (Ghosts).

Diffraction.—When a narrow illuminated slit is viewed through a glass grating, the lines of which are parallel with the edges of the slit, a bright image of it is observed with a series of spectra on each side; the violet rays with the shortest wave-length are nearest, and the red rays most distant, from the centre in each spectrum, and, if the colors are almost equally dispersed, the yellow will be found in the middle. The spectra are distinguished as of the first, second, . . . *m*th order, counting from the centre. The spectra of the first order only are pure; the others are modified by the superposing of other spectra, but they may be separated by means of a small prism as described in the following chapter. The intensity of the illumination diminishes with ascending order of the spectra.

¹ Denkschriften d. Münchener Akad. (1822) 8. Gilbert's Ann. 74, 337.

The production of spectra by means of gratings is due to diffraction; part of the light traversing the spaces between the rulings continues in a straight line, but a portion is bent sideways, or refracted, by the sharp edges of the opaque parts. The explanation of this phenomenon afforded by the wave-theory of light is as follows: The light-waves which fall on a fine slit cause the particles of ether present to vibrate; this motion is communicated to the neighboring particles and produces an equal number of light-waves which reinforce, weaken, or neutralize each other, in accordance with the law of interference. The neutralization occurs in all directions in which the difference between two sets of waves is other than a whole wave-length. In the case of white light, diffracted by means of a grating, the image of the slit, in the middle, is white because at this point all the colors are superposed, but the colored rays which differ in phase by one wave-length collect at each side according to their wave-lengths, and form a spectrum of the first order; those rays with a greater difference of phase forming the spectra of the second, third, . . . *m*th order.

The wave-length may be determined, if the distance between the lines of the grating is known, by measuring the angle of diffraction with a gonimeter. Ångström in this manner found the following values, in ten millionths of a millimetre, for the Fraunhofer lines given:

<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i> ₁	<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>
7604	6867	6563	5895	5269	4861	4307	3968

The dispersive power of a grating is dependent on the total number of the spaces into which it is divided, and on the order of the spectrum; in one of the first order 1000 lines per inch are necessary to separate the *D*-lines, whilst a large Rowland grating, in a spectrum of the first order, is capable of dividing two lines differing in wave-length by only 0.05 of an Ångström.

Comparison of the Diffraction and Refraction Spectra.

7 —Diffraction spectra differ from those produced by refraction in the dispersion of the rays being proportional to the wave-length, and this uniform extension applies although the dispersion increases with the number of lines on the grating. The refraction in the case of a prism spectrum increases with diminishing wave-lengths; the violet and blue rays are therefore comparatively widely separated, and the red ones gathered together. The length of the spectrum is also influenced by the composition of the prism, so that results obtained with different spectroscopes are not directly comparable; diffractive spectra are therefore taken as typical or normal, and all scale readings with a prism spectroscope are reduced to wave-lengths. The prism spectrum has the advantage over the diffraction spectrum of greater brightness, only a small proportion of the light is lost by reflection and absorption, whereas with the grating a portion of the light passes through without being diffracted, a portion is weakened by interference, and the remainder is divided amongst a number of spectra instead of being concentrated into one as in the case of the prism. The prism spectrum is therefore employed where the illumination is comparatively feeble, the grating being used for intense light and in cases where a high dispersion is necessary. A large Rowland grating in the region of the *D*-line produces the same effect as a prism 126 cm. in thickness; in the violet this proportion changes in favor of the prism; at $\lambda = 2000$ the same separation is attained by means of a prism only 4 cm. in thickness.

CHAPTER III.

SPECTROSCOPES.

THE numerous forms of instruments for spectrum analysis are all divisible into two classes, prism spectroscopes¹ with angular or direct vision, and grating spectroscopes.² The forms vary according to the special purpose for which the instrument is to be employed, such as exact measurements, quantitative and photometrical investigations, microscopical or astronomical observations, or for the preparation of spectroscopic photographs.

Prism Spectroscope with Angular Vision.—The apparatus employed by Kirchhoff and Bunsen³ in their earlier investigations is shown in Fig. 4. It consists of a hollow glass prism *F* filled with carbon bisulphide, of a telescope *C* magnifying eight times, and of the slit tube or collimator *B*, at the end nearest to the light; this is closed with a plate pierced with a fine slit; the other end contains a lens which makes the light-rays coming from *D* parallel before they fall on the prism. Shortly afterwards Steinheil of Munich con-

¹ For information on the theory of the prism in the spectroscope see Reusch, P. A. (1862) **117**, 241. Pickering, Sillim. Journ. (1868) **45**, 301. Christie, P. R. S. (1877) **26**, 9. Thollon, Journ. de phys. d'Almeida (1878), **7**, 141.

² For the theory of gratings see Rowland, P. M. (1892) [5] **13**; **16**, 197. Astronomy and Astrophysics (1893), **12**, 129. Ames, Johns Hopkins Univ. Circular (1889), **8**, No. 73, p. 69. P. M. (1889) [5] **27**. Runge, Winkelmann's Handb. d. Phys. (Breslau, 1894), p. 407. Glazebrook, P. M. (1889) [5] **27**. Mascart, Journ. d. phys. d'Almeida (1883) [2] **2**. Lord Rayleigh, P. M. (1874) [4] **47**.

³ Chem. Analyse durch Spectralbeobachtungen, P. A. **110**, 167.

structed for them an improved form of spectroscope (Fig. 5) which is still in use. A flint-glass prism *P* of 60° is fastened to a cast-iron stand which also carries the collimator-tube *A*,

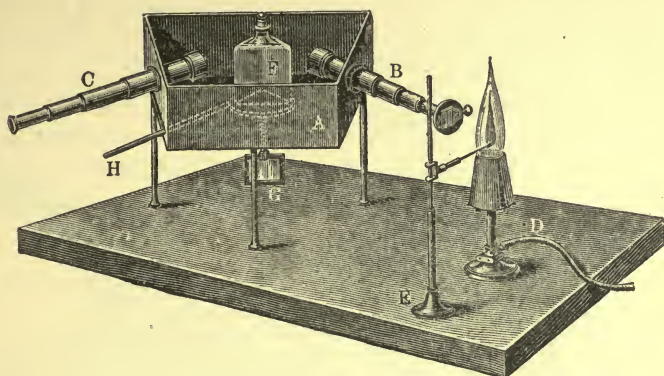


FIG. 4.

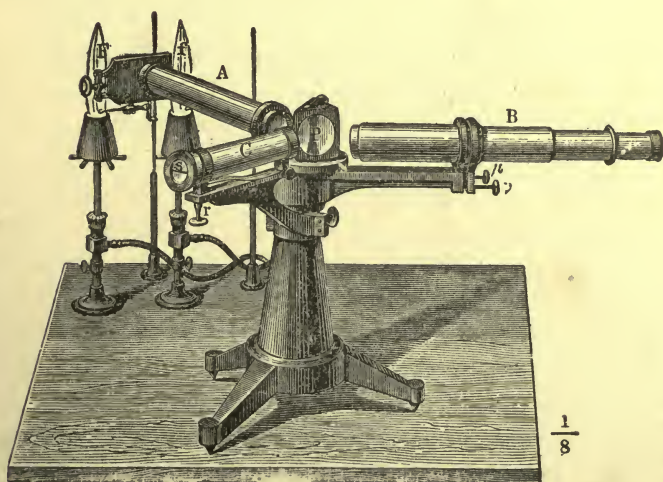


FIG. 5.

the telescope *B*, and the telescope *C* containing a scale. The mechanism for producing the slit carried by the collimator-tube is shown enlarged in Fig. 6. The width of the slit can

be regulated by a micrometer-screw; on the lower end a small reflecting prism (Fig. 7) is fixed, by means of which a second source of light, placed at the side, may be examined together with the first. With the apparatus arranged as in Fig. 5 the spectrum of the flame F appears above that of f , so that it is possible at a glance to see whether the former contains the substance sought, if a specimen of it is simultaneously volatilized in the latter. A millimetre-scale S is contained in the tube C ; it is illuminated by a small luminous flame, and

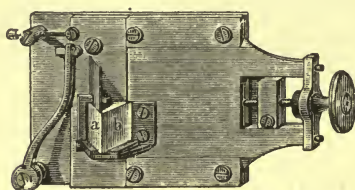


FIG. 6.

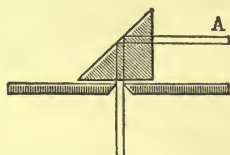


FIG. 7.

its image reflected by the adjacent side of the prism into the telescope B . In order to prepare such a spectroscope for use, the telescope B is detached, and adjusted to infinity by observing some fixed object at a considerable distance; if it contains cross-wires, these must be first focussed with the eyepiece; the telescope is then replaced, and the slit opened so that the spectrum lines are sharply defined, until, for instance, the sodium lines are resolved, and the scale-tube is drawn out to make the divisions clearly visible. In many modern instruments the length of the tubes A and C is adjusted to their lenses before they are sent out, so that only the eyepiece requires focussing by each individual observer.

The clearness of a spectrum is considerably influenced by the slit apparatus. The manufacture of these has greatly improved in the course of time, in finish, in the opening mechanism, and in the permanency of the material employed; the best substance for the edges is quartz, but platinum or brass is generally used.

The spectroscope above described is suitable for chemical laboratories, but not for astronomical purposes, for which a greater dispersion is necessary; this may be obtained by the use of several prisms instead of one. The instrument made by Steinheil, and used by Kirchhoff in preparing his drawings of the solar spectrum, is shown in Fig. 8. It contains

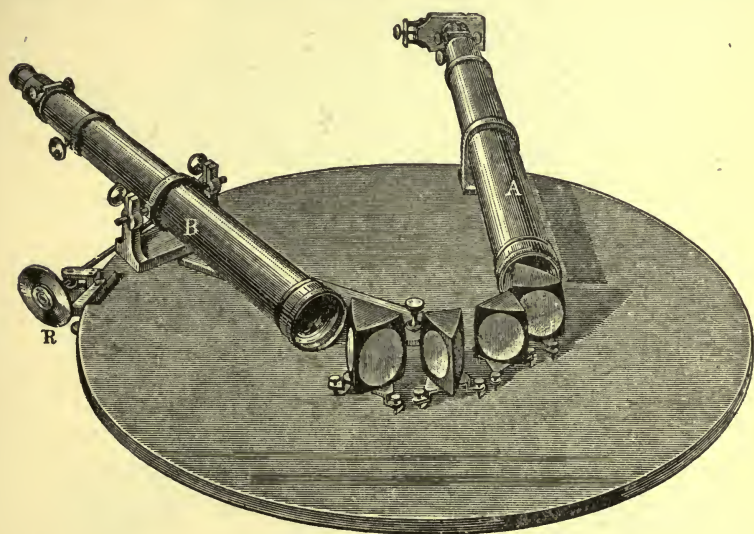


FIG. 8.

four prisms, and is at once simple and sensitive. The prisms are of flint glass with angles of 60° , 45° , 45° , 45° ; the light traverses them successively, and is refracted through 130° , so that the spectrum is greatly extended. The telescope *B* enlarges 36 and 72 times, according to the lenses employed, and moves on a divided circle by means of a micrometer-screw *R*; with the help of the cross-wires the distance between two lines may be readily measured; the slit is regulated by a sliding micrometer, and is provided with a comparison-prism.

The measurements may also be made with an illuminated scale in a second telescope (not shown in the figure); this is sometimes inconvenient, as the spectrum is so much longer

than the scale that the latter requires frequent readjustment. In the above instrument the prisms are moved by hand into the position of minimum dispersion for any given color; this is unsatisfactory: the arrangement devised by Browning (Fig. 9) makes the adjustment automatic. The prisms are

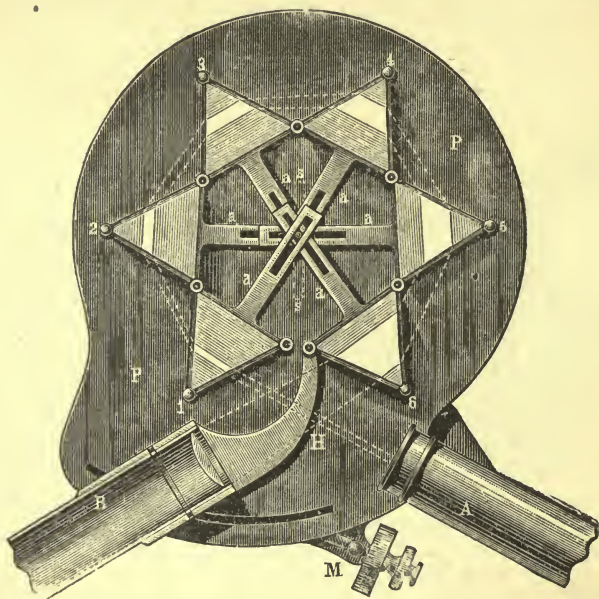


FIG. 9.

connected to each other, and to the observation-telescope, by hinges, and are fixed on metal plates the other ends of which are suitably cut to receive a central screw; on rotating the telescope *B* to any particular line in the spectrum, the prisms move with it, so that the ray traverses then symmetrically. Gassiot's spectroscope, constructed by Browning on this plan, contained nine prisms and possessed high refractive power.

There are several other ways by which the dispersion may be increased; instead of using several prisms the light may be repeatedly passed through a single one, or hollow prisms filled with some liquid of high refractive power may be employed.

Acting on a suggestion of Littrow,¹ Grubb,² C. A. Young, and Lockyer caused the light to pass twice through the same

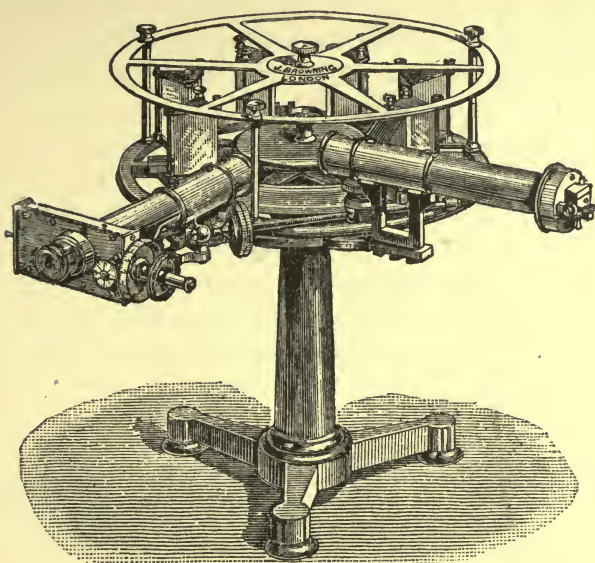


FIG. 10.

prism, as shown in Fig. 10. The ray passes first through the upper part of the prism and is then returned through the lower portion by means of a reflecting prism. The instrument shown is made by Browning; it is extremely powerful, and suitable both for laboratory and stellar work. It contains six prisms, besides the reflecting prism, and consequently the dispersive power is equal to that of twelve prisms. The position of any one prism can be altered at will, without interference with the other parts of the instrument, so that the dispersive power can be readily changed from two up to twelve prisms as required. The adjustment of the prisms to the position of minimum dispersion is made automatically in

¹ Wien. Ber. 47, 2, p. 26.

² Monthly notices of the Roy. Astron. Soc. 30, 36.

the manner described above; the position of the spectrum-lines is measured by means of a micrometer-screw, the movement of which also adjusts the prisms. Hilger of London constructed a large spectroscope in which the ray of light was passed six times through the same prism. The application of this method, and also the number of prisms which can be employed, is limited; the longer the spectrum the less bright any given portion must necessarily be. Moreover, the glass of which the prisms are composed is never absolutely homogeneous, nor the faces perfectly true; hence when many prisms are used there is a loss of clearness and definition. Ordinary prisms are greatly surpassed in dispersive power by the compound prism of Browning and of Rutherford,¹ which bears the name of the latter. It consists of a flint-glass prism

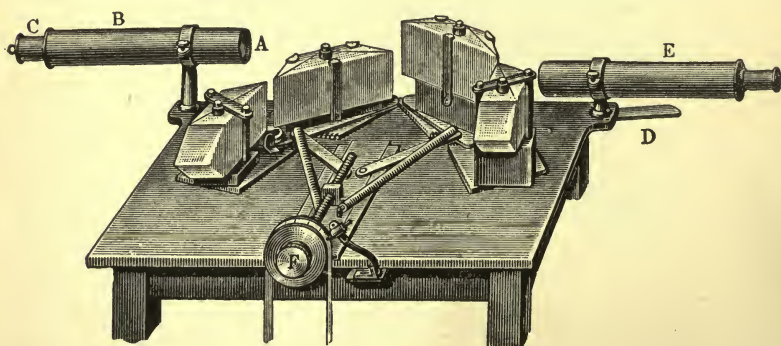


FIG. 11.

with its faces at such an angle that light which enters cannot emerge; in order to permit this, compensating prisms of crown glass, and therefore with a lower dispersive power, are cemented to each side face. This use of crown glass has comparatively little effect on the dispersion.

Thollon² constructed an instrument which, whilst probably

¹ Sillim. Journ. (1865) [3] 35, 71. 407.

² C. r. 86, 329, 395, 595; 88, 80; 89, 749.

unsurpassed in dispersive power, contains only a small number of prisms (Fig. 11). Its efficiency is due partly to careful calculation of the most suitable angles for the faces of the prisms, partly to their being filled with carbon bisulphide, which has a high refractive power (comp. preceding chapter). Only compound prisms are used, one of which is shown in Fig. 12. The refractive angle of the inner flint-glass prism is 90° , that of the carbon bisulphide prism 113° , and of the crown-glass prism 18 and 31° respectively. The light passes from the collimator *CBA* through the compound prism *A* (Fig. 13), then through the half-prism *B*, to the reflecting

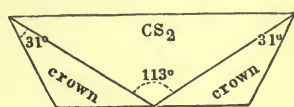


FIG. 12.

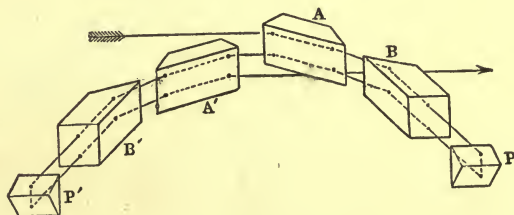


FIG. 13.

prism *P*; it now returns at a lower level, traversing the symmetrically arranged system *A'B'P'*, and finally emerges below the prism *A*. The telescope (*E*, Fig. 11) of this instrument is fixed, the prisms being movable, and maintaining the position of minimum dispersion. The screw *F* serves to rotate the prisms, and also a strip of paper, such as is used in the Morse telegraph-instruments; when a line is observed at the point of intersection of the cross-wires the lever *D* is pressed, causing the marker to record the position on the paper. Prisms containing carbon bisulphide are all subject to the disadvantage that its refractive power is greatly influenced by temperature, an increase of 0.1° C. being sufficient to alter the position of the lines to a distance equal to that between

the two sodium *D*-lines. It is therefore necessary, when using such prisms, to take care that the temperature remains uniformly constant. To accomplish this, Rayleigh, and also Draper, employ automatic stirrers. It has been proposed to replace the carbon bisulphide by other highly refractive liquids; Wernicke has suggested ethylic cinnamate, and Walter α -bromo-naphthalene as being suitable for this purpose.

Direct-vision Spectroscopes.—With the spectroscope last described the emergent ray travels at an angle with the entering one; instruments in which the slit, lens, prism, and telescope are in a straight line are termed direct-vision spectroscopes. They can be readily attached to a microscope or telescope, they are easy to handle and transport, are comparatively cheap, and the source of light can be viewed directly, so that these advantages over the ordinary form have led to their wide use for practical purposes where a great dispersion is not required. Amici in 1860 constructed a compound prism which almost permitted of direct vision; it consisted of a flint-glass prism of 90° , with a crown-glass prism on each side; Janssen¹ afterwards made a more elaborate system (Fig.

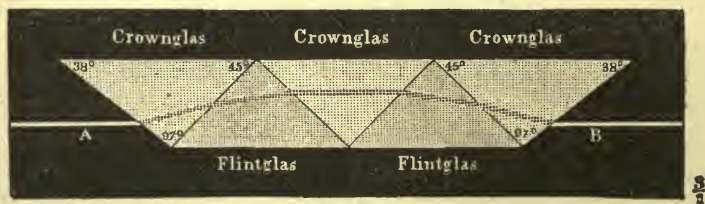


FIG. 14.

14), consisting of three crown- and two flint-glass prisms, which, whilst resolving the ray into its constituents, prevents its deflection. The spectrum from a flint-glass prism is almost double the length of that from a similar one of crown

¹ C. r. 55, 576.

glass, so that the dispersion is reduced by about one half in consequence of refraction in the opposite direction. It is only in a certain definite part of the spectrum, generally the green, that the incident and emergent rays follow the same path; the other portions are deflected to each side. The spectroscope constructed by Hofmann of Paris, under the

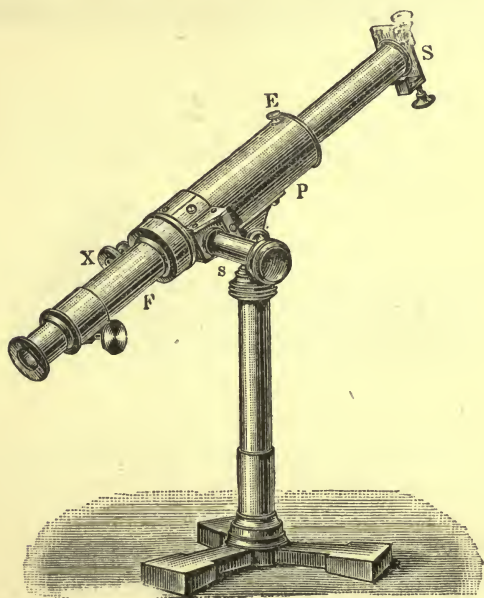


FIG. 15.

direction of Janssen, is shown in Fig. 15. The slit *S* of steel, is regulated by means of a screw, and has a comparison-prism; the tube *P* contains the lens *E* and a compound prism (Fig. 14); it is attached to the telescope *F*, which can be adjusted to any portion of the spectrum by the screw *X*. For most practical purposes a telescope is unnecessary. The instrument (Fig. 16) first constructed by Browning of London is very convenient, and is widely used; it is known as the direct-vision, pocket, or miniature spectroscope. It consists

of the slit *S*, the size of which can be regulated by turning the cap *s*, the lens *C*, and the compound prism *P*, composed of four crown- and three flint-glass prisms; the eyepiece *R*

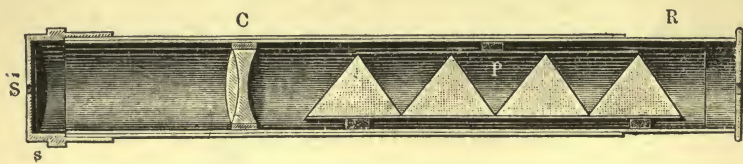


FIG. 16.

is adjustable. Another form of the same instrument (Fig. 17), also made by Browning, carries a detachable comparison-



FIG. 17.

prism and a photographed micrometer-scale, which, together with a biconvex lens, is contained in a small tube fixed parallel with the larger tube by a slot attachment; a reflection-prism throws the image of the scale on the outer surface of the last member of the compound prism, whence it is reflected into the eye of the observer. The instrument is only 8.5 cm. in length, and when in use is attached to a readily adjustable stand. Pocket spectroscopes similar to the simpler Browning form are manufactured by all instrument-makers. Guided by H. W. Vogel,¹ Schmidt and Haensch of Berlin construct an instrument which, instead of the scale, has a small rotatable mirror; the light from this is projected on to a reflecting prism, and thence to the upper portion of the slit. The mirror and comparison prism can be readily disconnected.

¹ Ber. 9, 1645; 10, 1428.

The majority of the above spectroscopes give a field extending only from the *A*- to the *G*-line; the violet portion is almost completely absent. Adam Hilger of London constructs a direct-vision spectroscope which, whilst somewhat longer than the others, is characterized by a high dispersive power. The spectrum extends from the extreme red beyond the *H*-line, shows the two *D*-lines, and, when directed at the sun, the nickel lines between them. The instrument is fitted with an achromatic eyepiece, and a special arrangement which reflects a slender line of light on to the spectrum to serve as a means of measurement; as the color and intensity of the line can be regulated, it permits, particularly in the darker portions of the spectrum, of far more accurate determinations than could be made with cross-wires. The measuring is performed with the help of a micrometer-screw attached to the slit, which it moves from end to end of the spectrum.

Amongst other direct-vision spectroscopes¹ Christies'² deserves mention on account of peculiarities in its construction. He employed "half-prisms," which are so called because they may be regarded as the halves of a tripartient compensating prism; the refracting angle may vary: if it is 90° , a long enlarged direct-vision spectrum is obtained, but the dispersion is not correspondingly great, and the illumination is poor. Hitherto it has only been used in England.

Grating Spectroscopes.—The advantages of diffraction-spectra have been already numerated, and it was mentioned that the grating spectroscope can only be used where the light is extremely bright, as in the case of the sun and electric arc, since the loss of light is considerable. The instrument is usually employed in the form of a spectrometer, of which one variety is shown in Fig. 20. The gratings are of glass or metal, the latter being preferable for exact

¹ Alex. Herschel, *Monit. scientif.* **7**, 259. Emsmann, *P. A.* **150**, 636. Kessler, *P. A.* **151**, 507. Fuchs, *Zeitschr. f. Instrumentenkunde*, **1**, 352.

² *P. R. S.* **26**, 8.

work. The general plan of a spectrometer is shown in Fig. 18. The grating *m* is at right angles with the collimator

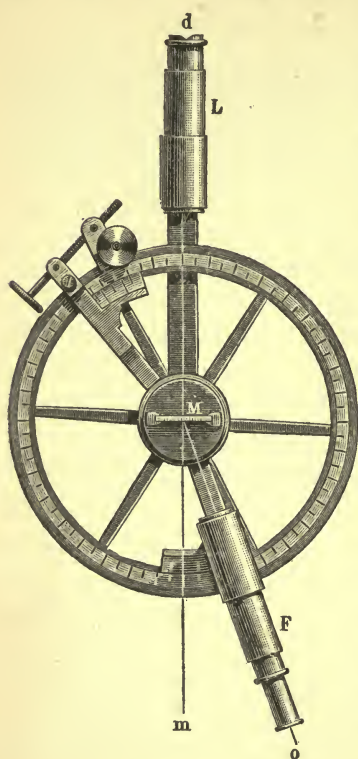


FIG. 18.

L, and secured to the bed of the instrument; the telescope *F* is fitted with cross-wires, and situated at right angles with the axis of the instrument. The telescope is directed towards the slit *d*, and its position read off on the divided circle; homogeneous light, such as the sodium flame, is then allowed to fall on the slit, and the telescope rotated until the spectra of the first, second, and third order are successively brought into the field of view, each position being noted; the wave-length of sodium light being accurately known, the readings provide a means of measuring the wave-length of any other kind of light, since the wave-length of the latter bears the same proportion to that of sodium light as the corresponding scale readings.

The wave-length can also be directly determined if the grating-constant is known; this is effected by counting under the microscope the number of lines in 1 mm. It was with such an instrument that Ångström made his celebrated determinations of the lines in the solar spectrum.

A simple form of spectroscope with a reflex grating is shown in Fig. 19. The telescope and collimator are situated close together on separate mountings; the grating is enclosed in a case with a plane parallel glass front to protect it from

corrosive fumes, and is fixed on a revolving stand so that spectra of any desired order can be brought before the cross-wires of the telescope. The spectra of higher order overlap, but they may be easily separated by following Fraunhofer's suggestion, and placing a prism between the grating and tele-

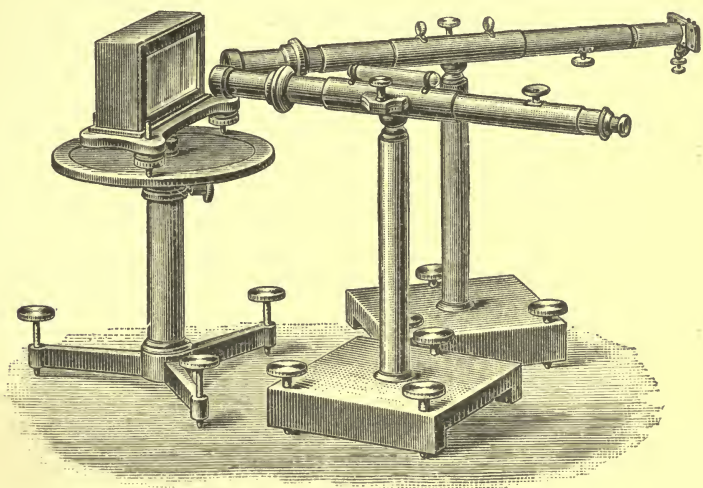


FIG. 19.

scope in such a position that the plane of refraction is at right angles to that of the grating; the spectra then appear clearly one above another, and can be separately observed.

Rowland's Concave-grating Spectroscope.—The development of spectrum analysis received a considerable impetus from Rowland's discovery of the concave grating in 1881. By its use measurements have attained a degree of accuracy otherwise unapproachable, and whilst this is specially true of the values obtained by the coincidence method, it also applies to wave-lengths directly determined; it is the only instrument which is available for use with all rays, including the ultra-violet and the infra-red, and, as no lens is necessary between the slit and eyepiece, defects from loss of light or spherical aberration are avoided; the gratings being astig-

matic. a luminous point, such as a spark, appears in the field of view as a line, thus greatly facilitating the comparison of solar lines with those of metals, and the enlargement of spectra. Photographs, both of the visible and invisible portions of the spectrum, are easily obtained, and their accuracy is necessarily far in excess of the drawings prepared from ocular observation; as it is generally used in conjunction with a camera, its detailed description is reserved for the following chapter. When employed for ocular purposes, the camera is replaced by a cross-wires and micrometer; with a highly accurate screw of 125 mm. the measuring arrangement resembles a dividing-machine in exactitude rather than an ordinary micrometer. The use of an eyepiece with a focal length of $\frac{1}{2}$ inch gives results equalling those obtained with a plane grating in combination with a telescope enlarging 100–200 times.

CHAPTER IV.

SPECTROSCOPIC INSTRUMENTS FOR SPECIAL PURPOSES.

Spectrometer.—This instrument is employed when exact measurements are required in spectrum analysis, the coefficient of refraction being determined by the method of minimum dispersion. The numerous instruments on the market, whilst differing in detail, agree in principle; the one described here (Fig. 20) is constructed by Schmidt and Haensch of Berlin, according to the design of V. v. Lang. The stand can be adjusted horizontally by means of levelling-screws; it carries in the middle a pillar with a steel axis; in the centre at the upper end of this is a metal plate with a divided circle, at the lower end a clamp and six radial arms for the rotation of the axis; fitting over the central pillar is a stout bronze cylinder which carries the vernier circle at the top; an astronomical telescope with cross-wires and counterpoise is fastened to the side, whilst the clamping arrangement is attached below. The stand carries the micrometer-screws for the divided circle and vernier, and also the holder for the collimator, which is fitted with a lens, an adjustable slit, and a comparison-prism. Rising from the central pillar through the middle of the divided circle is a rod carrying a round plate, the height of which can be regulated; it also is divided, has a fixed vernier, and serves to support the prism or grating. The circle is enclosed in a case fitted with windows, so as to protect it from corrosion; both it and the outer vernier-circle can be rotated independently; to facilitate readings the tele-

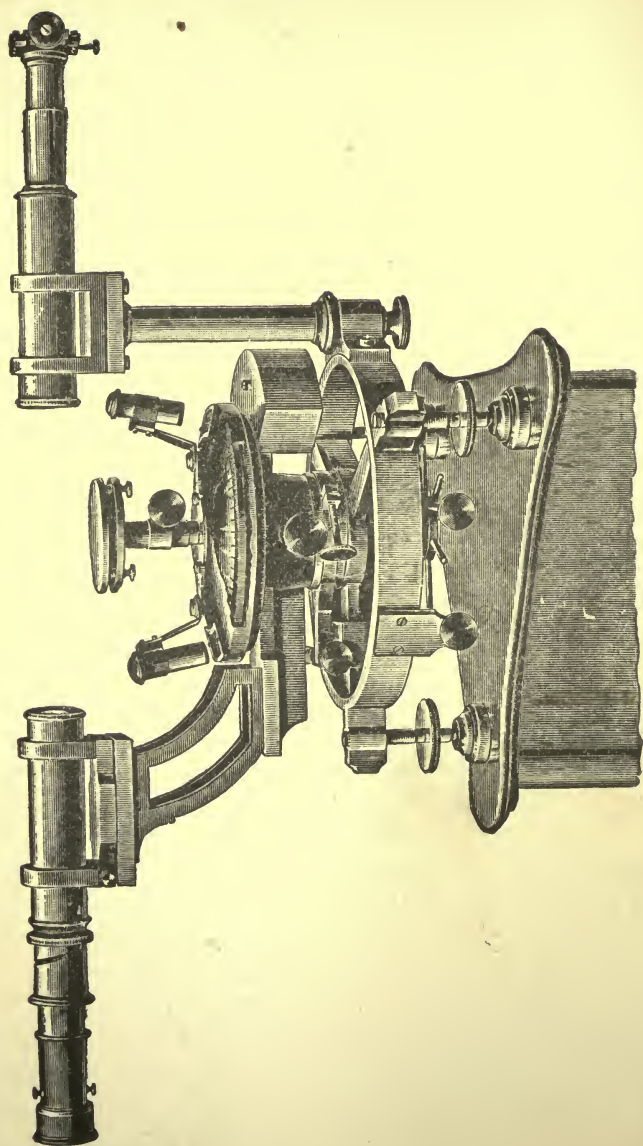


FIG. 20.

scope may also be moved without altering the position of the circle. The instrument is provided with a Gauss' eyepiece (Fig. 21), in addition to one of the ordinary form; it has an opening (*b*) at the side, which admits light to a plane parallel glass plate placed behind it at an angle of 45° with the axis of the telescope; the light is thus reflected on to the cross-wires. The correct orientation of the instrument is of considerable importance. The telescope is adjusted to infinity and placed at right angles to the axis of rotation, the cross-wires and eyepiece being in sharp focus; the collimator must also be adjusted to infinity and fixed at right angles to the axis of rotation, whilst the refracting edge of the prism is parallel with this.

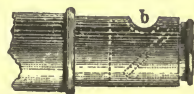


FIG. 21.

The refractive index (*n*) is calculated from the angle of refraction (*g*) and that of dispersion (*D*). In order to obtain the former, the telescope, fitted with the Gauss eyepiece, is adjusted at right angles to the first prism-face, and then rotated until it is at right angles with the second face; the reading obtained, subtracted from 180° , gives the refractive angle (*g*). The angle of dispersion (*D*) is determined as follows: The prism is removed, and the telescope with cross-wires directed on the slit—this gives the zero-point; the prism is then replaced in the position of minimum dispersion, and the telescope again adjusted towards the slit—the difference in the readings gives the angle of dispersion for the particular color. The coefficient of refraction is then calculated by the expression

$$n = \frac{\sin \frac{1}{2}(g + D)}{\sin \frac{1}{2}g},$$

and the wave-length of the refractive index *n* by Cauchy's¹ dispersion-formula

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \dots ;$$

¹ Mémoire sur la dispersion de la lumière (Prague, 1836).

for ordinary purposes the last constants can be neglected, as they are very small. A and B are obtained from the expressions

$$n_1 = A + \frac{B}{\lambda_1^2} \quad \text{and} \quad n_2 = A + \frac{B}{\lambda_2^2},$$

which necessitate the determination of the refractive indices n_1 and n_2 of the prism for two rays, the wave-lengths λ_1 and λ_2 of which are accurately known, such as two prominent Fraunhofer lines.

Krüss' ¹ Universal Spectroscope.—This instrument is manufactured by A. Krüss of Hamburg from the design of G. Krüss;¹ it is suitable for all kinds of spectro-chemical investigation, and admits of measurements being made which in accuracy closely approach those obtained by the spectrometer. In its general plan the instrument (Fig. 22)

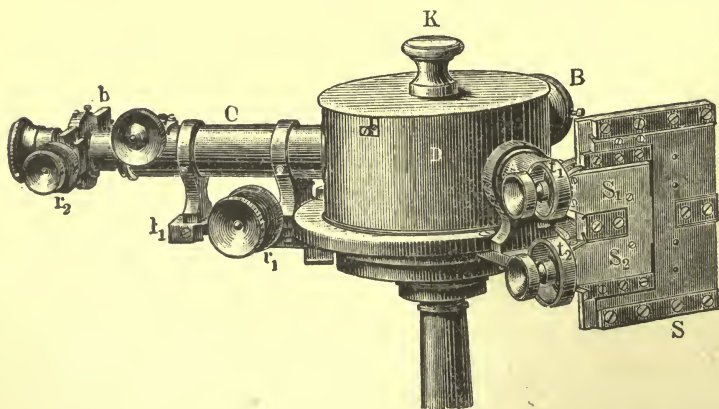


FIG. 22.

resembles that of Bunsen and Kirchhoff; the telescope magnifies seven times; the tube B carries the scale, which is fixed in the focus of the objective; the 100 division is adjusted to correspond with the middle of the D -lines; the slit on the collimator A is likewise sharply in the focus of the objective,

¹ Ber. 19, 2739.

and parallel with the refracting edge of the prism. Two different slits are employed, a single one for qualitative, and a double one for quantitative analysis; in the case of the latter both slits open symmetrically to the optical axis, so that with apertures of all sizes the spectra retain the medial position. The single slit is provided with a detachable comparison prism, and its width regulated by a micrometer screw with a divided milled head. The halves S_1 and S_2 of the double slit S may be separately adjusted by means of micrometer-screws with the divided milled heads t_1 and t_2 . Two prisms are provided, one of flint glass of low dispersive power with an angle of 60° , and a highly refractive Rutherford prism; they are contained in the case D , and are retained in the position of minimum dispersion by the pressure of a spring under the knob K . The measuring appliances are attached to the telescope, which, together with its holder, may be rotated around the vertical axis of the instrument by a micrometer screw with a milled head r_1 divided into 100 parts; complete revolutions of this are read off on a divided scale directly under the eyepiece. The cross-wires are moved independently by a similar screw with its milled head r_2 also divided into 100 parts. These arrangements permit of accurate measurements of spectra; and as the relationship of the screw-threads to each other and to the divisions of the scale are known, the measurements made by any one can be doubly controlled.

Spectrophotometer.—A special peculiarity of the preceding instrument is the double slit, first employed by Vierordt¹ in his photometric work with absorption-spectra and quantitative spectrum analysis. To determine the quantity of a colored substance in solution it is poured into a trough or a Schultz's glass, and placed in front of one slit; the other is then closed until both are of equal brightness; the move-

¹ P. A. 140, 172. Die Anwendung des Spectralapparates zur Photometrie der Absorptionsspectra und zur quantitativen Analyse (Tübingen, 1873).

ment of the slit is measured by the divided screw-head, the amount of light cut off being equal to that absorbed by the quantity of substance in solution. In Glan's,¹ and Hñfner's² spectrophotometers the diminution of the light is not determined by closing the slit, but by polarization.

Sorby's Microspectroscope.—It is often desirable to apply the spectroscope to the investigation of microscopic objects, such as rock sections, leaves, the sap of plants, opaque substances, and for the identification of the coloring matter of blood in medico-legal cases. For this purpose Sorby,³ in conjunction with Browning, arranged a convenient combination of microscope and spectroscope. The instrument (Fig. 23) is inserted into the tube of a microscope instead of the ordinary eyepiece; the rays proceeding from the lens pass successively through the slit, the combining lens, and an Amici compound prism; at right angles is placed a measuring arrangement consisting of a ray of light from a mirror which is reflected into the eye of the observer by the exterior face of the last prism; a dark photographed background is provided, and a delicate micrometer-screw which enables the ray to be accurately adjusted to any spectrum or absorption line. A second mirror serves to illuminate the comparison-prism, and a small stand at the side on which objects can be fixed. Light for the mirrors is obtained from a single lamp.

A modification of this microspectroscope devised by Abbe and constructed by C. Zeiss of Jena is shown in Fig. 24. The screw *M* fixes it in the tube of the microscope in such a position that both the mirrors *A* and *O* are illuminated by the sun. The upper portion, containing the prisms, can be rotated round the peg *K* so as to admit of the object being adjusted; when this is accomplished the prisms are turned until the closing of the catch *L* indicates that they are in position.

¹ W. A., 1, 351.

² J. pr. Chem. [2], 16, 290. Zeitschr. f. phys. Chem., 3, 562.

³ C. N., 15, 220. P. R. S., 15, 433.

The mirror *A*, indicated by dotted lines, illuminates objects fastened to a stand at the side; the light passes through an opening to the comparison-prism, which is fastened to the slit

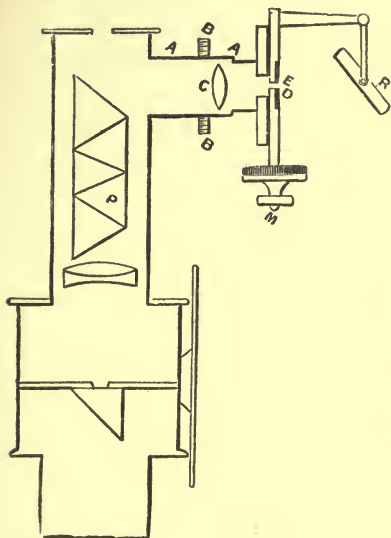


FIG. 23.

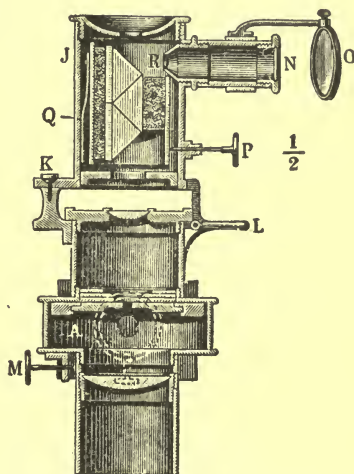


FIG. 24.

and is not shown in the figure. A peculiarity of the instrument is found in the measuring arrangement: the scale *N* gives the wave-lengths, in parts of a micromillimetre, of the region of the spectrum, coincident with its divisions; the compound prism is fixed between pieces of cork, and can be inclined from the vertical by means of the spring *Q* and the regulating-screw *P*, so that the divisions of the scale may be made to correspond exactly with the Fraunhofer lines; the mirror *O* reflects the scale on to the exterior prism-face.

Solar and Stellar Spectroscopes.—The extensive application of spectrum analysis to astronomical purposes has resulted in the designing of a very large number of instruments suitable for such observations. Solar investigations are generally carried out with fixed apparatus, grating spectroscopes,

spectrometers, and angular-vision spectroscopes of high dispersive power, the light being supplied by means of a heliostat. The solar prominences could formerly only be observed during an eclipse, but Lockyer and Janssen simultaneously devised a method by which they may be investigated at any time. For this purpose a spectroscope of high dispersive power is required; it is connected with a telescope, and the slit of wide aperture directed tangentially to the solar limb. Any spectroscope of high dispersive power may be employed for this purpose, if it admits of rotation around the collimator-axis so as to discover the prominences. It is not easy to securely fasten a heavy spectroscope to a telescope; for this purpose a special form of stand, termed an adapter, has been described by H. C. Vogel, but it is highly desirable that the spectroscope should be as light as possible. Such a

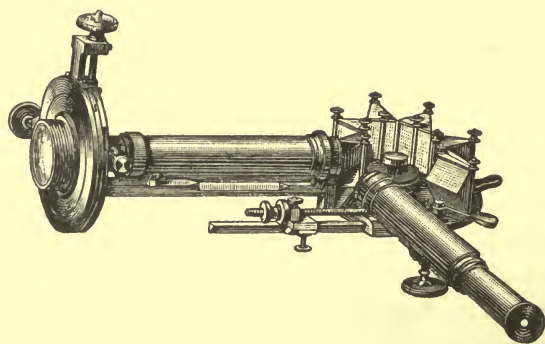


FIG. 25.

solar spectroscope, designed by Browning, is shown in Fig. 25; an arrangement is provided by which it can be screwed on to the eyepiece of a refractor of three or more inches diameter. The screw-ring carries a position-circle, divided into whole degrees, the pointer (alidade) of which has two adjustable bars at right angles; to the front one are attached the supports for the collimator and prism-plate. The collimator and telescope are fixed, the five prisms move automatically; a

reflection-prism causes the rays to return through the system, so that the effect of ten prisms is obtained. The measuring arrangement is on the left of the telescope; it consists of a triangular brass rod with a micrometer-screw by means of which the prisms are automatically adjusted to the position of minimum dispersion for the particular ray under examination. The instrument shows six lines between the two *D*-lines with the sun at its brightest. Since the dispersive power can be varied from two to ten prisms, the instrument can also be used for stellar and other celestial observations, where, in consequence of the feebleness of the light, a lower dispersion is required.

For a general survey of the sky, or for the observation of fixed stars which appear as points, a telescope may be attached to a direct-vision spectroscope without a slit; such instruments have been designed by Zöllner, Secchi, H. C. Vogel, McClean, v. Konkoly, and others, but they are not adapted for accurate measurement.

For the investigation of the spectra of meteors, v. Konkoly recommends a direct-vision spectroscope with a concave cylindrical lens attached to a small telescope; the field of view then includes about 27° , and the rapid motion of the meteorite is apparently diminished.

Stellar Spectrometers.—H. C. Vogel has designed a good spectrometer which is fastened to a telescope, and permits of accurate stellar spectroscopic measurements being made. More recently Adam Hilger of London has constructed an instrument specially adapted for solar and stellar work, and it can also be mounted on a stand for use in the laboratory.

Spectrographs.—The use of a combination of spectroscope and photographic camera, termed a spectrograph, has led to extremely valuable results: errors of observation and drawing are avoided; records are obtained of the invisible infra-red and ultra-violet regions, and also of celestial objects,

the light from which is too feeble to affect the eye, and necessitates a prolonged exposure. H. W. Vogel¹ has designed a large and a small form of this instrument; the latter has a wedge-shaped slit, a collimator-lens, an Amici prism of five members, and an aplanatic lens which throws the image on the ground-glass or sensitized plate at the back of the camera. The larger instrument is adapted for deflected rays, has two prisms of 60° , and is rotatable around both the vertical and horizontal axes, which permits it to be used for solar and terrestrial purposes. Ostwald² has suggested the following procedure for the photography of absorption-spectra: A horizontal plate is screwed on to the objective of a photographic camera, to which a spectrometer-prism and collimator-tube containing the lens are attached; the spectrum is thrown on the ground-glass plate by a Luter's aplanatic lens of 40 cm. focal length, and brought to accurate focus by observation of the solar lines. The prism employed has a refracting angle of 60° , and is filled with α -bromonaphthalene;³ its dispersive power is especially high in the ultra-violet. An Auer incandescent gas-lamp is recommended as the source of light.

Photographs of stellar spectra are obtained by attaching the spectrograph directly to a telescope. The large spectrograph at the Astrophysical Institute at Potsdam⁴ is an example of such an instrument; it gives extremely accurate reproductions of stellar spectra. The ocular of an eleven-inch refractor is removed, and a strong stand attached in its place; to one end the spectrograph is screwed; the collimator-tube of this, in order to insure stability, is sustained on a conical steel holder with an adjusting arrangement and a scale. Next to the collimator is a stout circular holder for the two Rutherford prisms of high dispersive power; beyond this is a conical

¹ P. A. 154, 306; 156, 319.

² Zeitschr. f. phys. Chem. 9, 579.

³ Walter, W. A. 42, 511.

⁴ Scheiner, Spectralanal. der Gestirne (Leipzig, 1890), p. 107.

camera which, to guard against vibration, is attached by stays to the far end of the collimator-tube. The collimator and object lenses are achromatic to chemically active rays. About 40 cm. from the slit, in the focus of the refractor objective, is placed a Geissler's tube containing hydrogen; this serves to illuminate the slit, and also affords a means of measuring the displacement of the lines caused by the motion of the star across the field of view, since the photograph shows the stellar spectrum together with the $H\gamma$ -lines. The refractor is set in motion so as to maintain the middle of the slit exactly on the star. Bromo-silver gelatine plates are usually employed.

Rowland's Concave-grating Spectrograph.¹—The merits of this instrument have been enumerated in the preceding

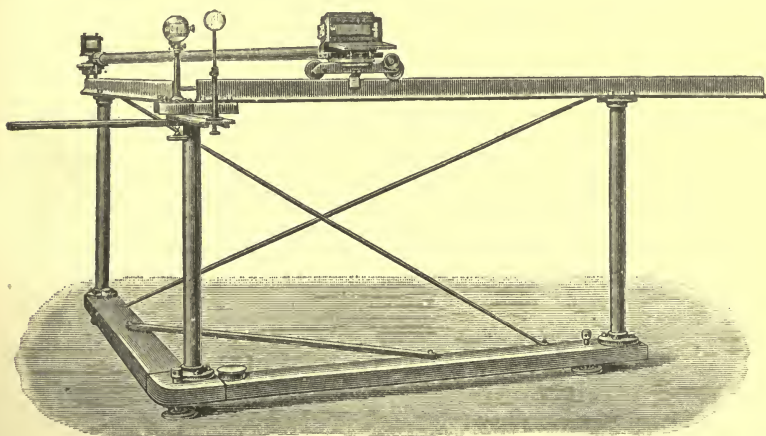


FIG. 26.

chapter; its separate parts require special arrangement, for, as Rowland has pointed out in his theory of the concave grating, normal spectra are only obtained if the slit, grating, and camera, or eyepiece, are placed in the periphery of a

¹ P. M. [5] 16, 197. *Astronomy and Astrophysics* (1893), 12, 129. Johns Hopkins University Circulars (1889), 8, No. 73, p. 73. Ames, *ibid.*, 8, No. 73, p. 69. P. M. (1889) [5] 27.

circle of which the grating forms a segment; the diameter of the circle is dependent on the concavity of the grating. This adjustment is effected mechanically by means of two rods at right angles; the grating is placed at their point of intersection, so that it is always maintained at a constant distance from the camera. The external appearance of the instrument is shown in Fig. 26. Fig. 27 exhibits the plan of the one

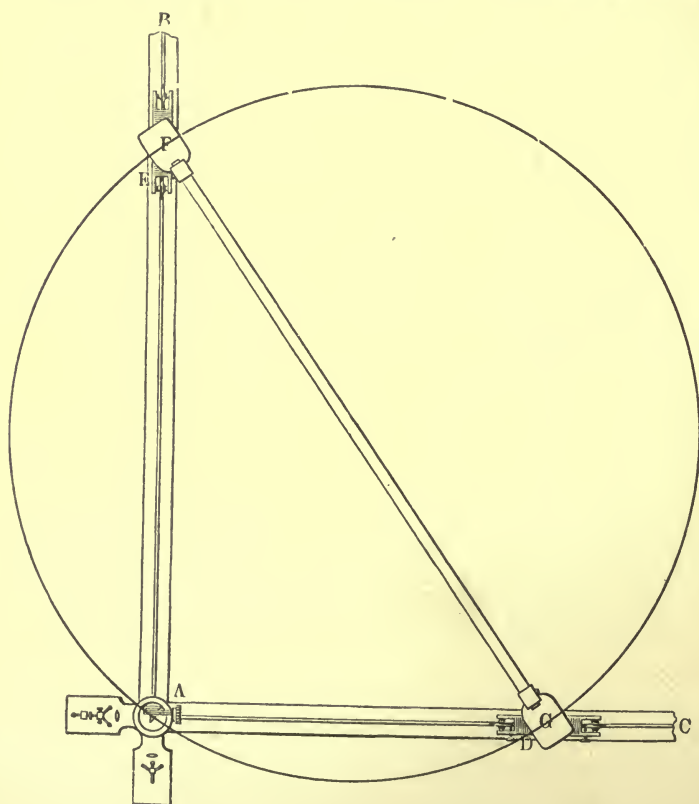


FIG. 27.

employed by Rowland for his classical measurements of the solar lines. It consists of two stout wooden beams AB and AC , 15×33 cm. and 7 metres in length; one is fixed, but

the other is slightly movable, by means of screws, about the point *A*. The beams are provided with rails for the wheels at each end of the carriages *D* and *E*; apertures are cut in these exactly coincident with the rail to receive the peg of the transverse beam *FG*, which is made of 4-inch wrought-iron tube; its length corresponds with the concavity of the grating, and, in the case of a six-inch grating with 110,000 lines, is about 6.55 metres, with 15 cm. for adjustment. The grating is fixed

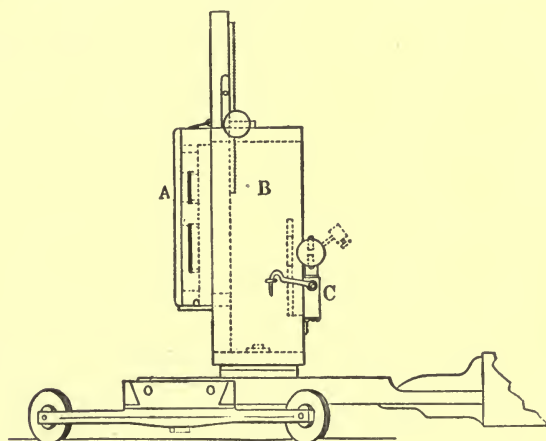


FIG. 28.

to *D*, and the camera to *E*; the latter is shown in Fig. 28. It consists of the fixed box *B*, and the movable case *A* to hold the photographic plate, which is bent to the desired form by pressure against a rubber pad; the wooden rod *C* carries a brass plate with a long narrow opening; it is rotatable about its horizontal axis, and is used to obtain a comparison-photograph. The sensitive plates are 48×5 cm., and 1.8 mm. in thickness; the breadth of the spectrum varies according to the order, from 6 mm. to 10 cm. The grating-holder is shown in Fig. 29, and consists of a massive bed-plate *A*, and a movable perpendicular frame *B*; to this a brass rod *D* is fastened by the screw *P*, and is movable about this axis by the

screw *S*; a second movable frame is attached to the brass rod by means of the screw *P*, and is rotatable about *P'* by the

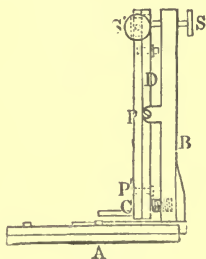


FIG. 29

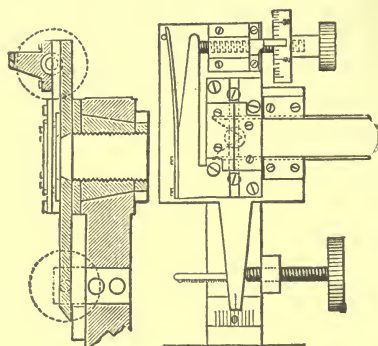


FIG. 30.

screw *S'*; it carries the grating, supported on two projections, and fixed by wax so as to be quite free from pressure. The orientating-screws work against springs so that the grating is readily movable in any direction. Gratings of varying diameter are used with 10,000 to 20,000 lines to the inch; for most purposes the first is sufficient, but the last is preferable for work with the ultra-violet rays. The slit (Fig. 30) must be capable of being raised, lowered, and rotated about its horizontal axis; the latter is of special importance, as a sharp image can only be obtained if the slit and lines are exactly parallel. The aperture is regulated by means of a micrometer-screw; as a rule its width is only 0.025 mm. The light from the electric spark or arc, or from a heliostat if the solar spectrum is being examined, is directed on a convergent quartz lens in the focus of the slit, whence it passes directly to the slit; if the source of light is at the side, a reflecting prism is employed. The astigmatism of the grating precludes the simultaneous photographing of a spectrum and a superposed comparison-spectrum, as with the prism-spectroscope; the comparison-photographs are therefore made separately, but on the same plate. By means of the arrangement at the back

of the camera, the comparison-spectrum is received in the middle of the plate, and the spectrum under examination above and below. A triangular stand placed between the slit and the quartz lens serves to support vessels containing absorbent solutions to cut off the spectra of other orders which would otherwise obscure the one employed.

These concave-grating spectroscopes, of excellent finish, are manufactured by John A. Brashear of Allegheny.

By means of Rowland's coincidence method a knowledge of one absolute wave-length enables all others to be determined, relatively to this, with an extremely high degree of accuracy.¹ Taking D_1 as the basis, it is photographed in the spectra of as many orders as the grating permits; the other orders are thus obtained simultaneously on the same plate, viz., D_1 in the first order, 2948 in the second, and 1965 in the third; with D_1 in the second order, 3931 in the third, 2948 in the fourth, 2358 in the fifth, etc. The following table gives the coincidences with D_1 in the first nine orders:

1	5896					
2	2948	5896				
3	1965	3931	5896			
4		2948	4422	5896		
5		2358	3538	4717	5896	
6		1965	2948	3931	4913	5896
7			2527	3369	4211	5054
8			2211	2948	3685	4422
9				2620	3275	3931

The distance between the D_1 -line and separate lines of these different orders is measured, and the wave-lengths approximately calculated from the grating constant, which is known with a fair degree of accuracy, and its concavity; if the wave-length of the lines does not differ by more than 50

¹ Comp. Kayser, A. B. A. 1890.

Ångströms from that of D_1 , a result is immediately obtained, correct within 0.5 of an Ångström. The accuracy of this result may be increased to any desired degree; if, for example, the wave-lengths 4422 and 4717 ± 0.5 are photographed on a plate, and their distance measured, the result is accurate to one third per cent, since their difference of 300 units is known to be exact to one unit; with this higher approximation the calculation is repeated, giving data of still greater accuracy, and so on.

Rowland obtained his system of wave-lengths in this manner; between $\lambda 2400$ and $\lambda 7000$ it is exact within at least 0.01 Ångström, and, together with his atlas of the solar spectrum, it forms the basis of all spectroscopic measurements.

CHAPTER V.

SPECTROSCOPIC ADJUNCTS.

Flame-spectra.—The flame of a Bunsen burner is sufficient to volatilize compounds of the metals of the alkalis and alkaline earths; for compounds of these metals which are particularly difficult to vaporize a Terquem burner may be used, as recommended by Wiedemann and Ebert. The flame, spectra of many substances can only be obtained by the use

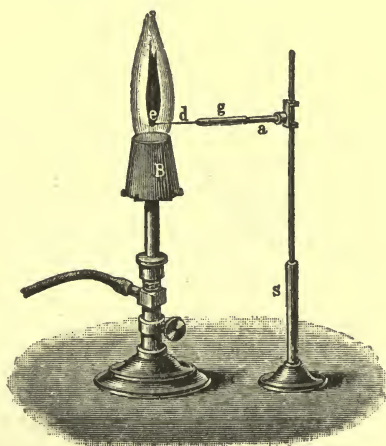


FIG. 31.

of a blowpipe, hydrogen, or oxyhydrogen flame, all of which were employed by Kirchhoff and Bunsen. A Barthel or other suitable spirit-lamp may take the place of a gas-burner if necessary. In many cases a relatively cool flame is desirable; this can be obtained, according to Salet's suggestion, by placing the gas-flame in contact with a plate of marble or metal, the opposite side of which is kept cool by means of a

stream of water. The substance is brought into the flame on a platinum wire; one end is bent to a loop, and the other is fused into a small piece of glass tubing which is fastened to the arm of a Bunsen stand (Fig. 31). Mitscherlich's apparatus is employed when a flame-spectrum is required during a considerable period of time. It consists of a series of glass

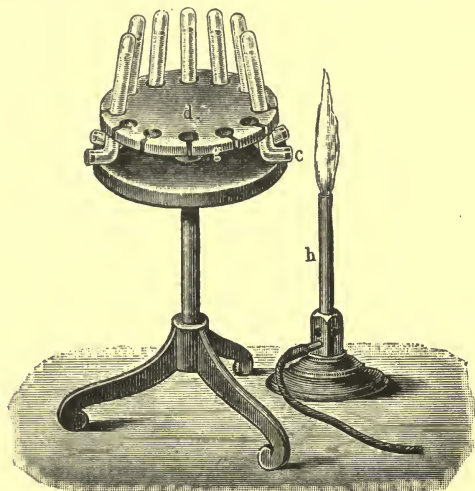


FIG 32.

tubes (Fig. 32) closed at the upper end; the lower end is bent, and filled with a bundle of slender platinum wires or threads of asbestos *c*; the substance under examination is dissolved, a little hydrochloric acid or ammonium acetate added, to prevent the formation of crusts on the wires, and the solution placed in the tubes. Gouy's¹ method consists in causing the air or gas, before it reaches the burner, to pass through a vessel containing the substance in solution or in a very finely divided state. Neither of these arrangements is satisfactory when a uniformly bright flame has to be maintained during

¹ A. c. p. [5] 18, 25. The construction of the pulverizing apparatus is described in Ebert's work *Anleitung zum Gasblasen* (Leipzig, 1895, 2d ed.), p. 59.

several hours; for such purposes Eder and Valenta's¹ apparatus (Fig. 33) can be employed. It consists of a heavy metal pedestal *P*, rotatable about its vertical axis; the Bunsen or Terquem burner *b* is fitted with a platinum ring; the wheel *s* is adjustable, and inclined at an angle of 45° : it consists of two nickel plates carrying a circle of platinum gauze *n*, which projects 2–3 cm. beyond the circumference of the wheel, and

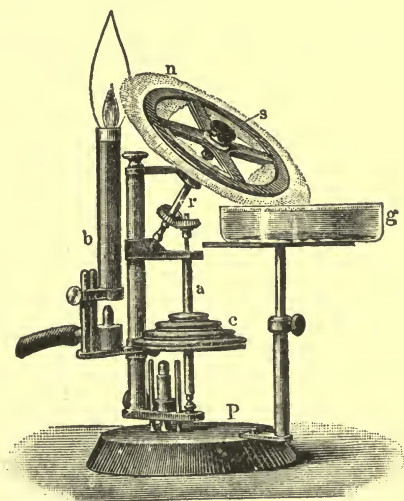


FIG. 33.

dips into the vessel *g* containing the solution of the substance. The axle *a*, connected with the cone *c*, permits of the rotation of the wheel by clockwork or some suitable motor. Mitscherlich,² Wolf and Diacon,³ and Salet⁴ place readily volatilizable substances in a glass tube fused to the hydrogen generator, and heat them in the gas which is then burnt at a platinum jet fused to the other end of the tube. For pro-

¹ Denkschr. der mathem.-naturw. Classe der Wien. Akad. (1893) 60, 468.

² P. A. (1863) 121.

³ Mém. de l'Acad., Montpellier, 1863.

⁴ A. c. p. (1873) [4] 28. Spectroscopie (Paris, 1883).

longed observations on haloid compounds of metals, the coal-gas must be mixed with chlorine, bromine, or iodine vapor.

The Bunsen burner gives a temperature of about 2300° , and none of the others are hot enough to show more than a comparatively small number of spectra; the electric arc and spark are of much wider application.

The Electric Arc.—The temperature of the arc ranges from 3000° – 3500° (Violle), and is the most generally applicable of all methods of producing metallic spectra, as its high luminosity permits the use of gratings, and also renders it suitable for projection. Kayser and Runge employed it in their accurate measurements of the spectra of terrestrial substances; usually they used a current of 50 volts and 20–30 ampères, but occasionally, for the shorter wave-lengths, 40 ampères were required. The anode carbon is placed below, as it burns to a cavity which serves to receive the substance, and its temperature is higher than the cathode. In order to prevent the metal or salt from overflowing the cup, rods of not less than 2 sq. cm. are employed. The formation of oxide may be prevented by boring the upper carbon, and conducting a current of some gas through it, or, better, by the use of a block of gas-carbon, quicklime, marble, or magnesia as suggested by Liveing and Dewar.¹ The block is pierced completely through in two horizontal directions crossing at right angles in the middle; glass tubes carrying the carbon rods are fitted to two opposite openings; light is emitted by the third, and the fourth serves for the admission of gas (carbon dioxide or hydrogen); a fifth opening, immediately above the point of intersection of the others, is for the introduction of the substance. The arc plays on the body under examination and volatilizes it; Kayser and Runge recommend the use of a magnet to cause the arc to impinge directly on the substance below the opening. The apparatus is also

¹ P. R. S. (1879). Proc. Cambridge Phil. Soc. (1882) 4. Kayser and Runge, A. B. A. 1890, 1891.

useful for observing the reversal of the lines by absorption, as the opening through which the light passes is always full of comparatively cool vapor; the intensity of the lines is less with the block than when the substance is volatilized directly from the carbon rod. A series of carbon bands are almost always observed above the metallic spectrum when metals or salts are volatilized between carbon terminals; this often adds greatly to the difficulty of measuring the lines, and, in order to avoid error, an exact knowledge of these bands is necessary. The difficulty may be obviated by using terminals of the particular metal under observation, but this has other drawbacks: the lamp is no longer automatically regulated, as the glowing rods of metal fuse immediately they come into contact, whilst, if the arc is extinguished for a moment, the terminals become coated with oxide, which is a bad conductor, and requires to be scraped off.

The Electric Spark. — The spark from an influence machine or induction-coil may also be used for the production of luminous vapor; the spectra of gases are produced solely by its help, it is more convenient than the arc, and is therefore employed more frequently, although spark-spectra exceed those of the arc in complexity, and their nature is not at all clearly understood. The temperature of the spark varies between wide limits; E. Wiedemann¹ observed a temperature of 87,000° in a Geissler tube.

The induction-spark differs with the construction of the coil; if this is composed of a large number of turns of thin wire, a high potential is obtained, whilst with shorter and thicker wire the potential is reduced, and the quantity of electricity increased. The intensity of the discharge may be heightened by the use of more powerful primary batteries, by the introduction into the circuit of one or more Leyden jars, or by increasing the length of the spark-gap. It is usual to

¹ W. A. (1879) 6, 298.

connect the poles with a condenser as shown in Fig. 34. The wire $K'p'$ connects the outer coating of the jar L with one pole of the coil, whilst the other is joined with the spike T , whence the sparks pass to the plate P connected with the inner coating of the jar. The wires MK , $M'K'$ lead to the stand H , to which the metallic electrodes EE' are fastened, to

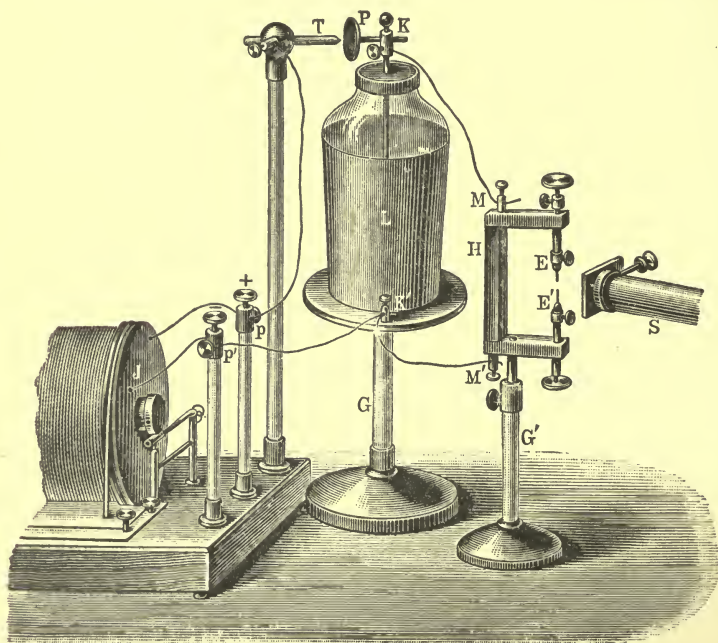


FIG. 34.

and the spark is produced between them. The intensity and quantity of the current can also be increased when an influence machine is used; the poles are connected in a similar manner with a Leyden jar, and the potential may be raised by prolonging the path of the spark.

The simplest means of obtaining the line-spectrum of a metal is to pass the spark between electrodes composed of it; particles are then detached and volatilized. The spectrum

of the atmosphere, consisting of the nitrogen, oxygen, and hydrogen lines, always accompanies that of the metal (comp. nitrogen, Chapter VII). In cases where a metal is not available, a solution of one of its salts may be used; this is made the cathode and the spark passed over it. Delachanal and Mermet's¹ apparatus is very convenient for use in this connection, as it permits the observation of the spectra during a considerable period. It consists of a glass vessel (*A*, Fig. 35), 15 mm. in diameter, with a platinum wire fused through the lower end, and connected with the cathode of the coil; over it is placed a conical capillary tube *D* projecting 5 mm. above the end. The upper part of the vessel is closed with a cork *C*, through which is passed a glass tube *B* with a platinum wire fused to it; the end *d* projects and forms the anode. The salt solution is added up to half the height of the cathode; it rises by capillarity to the end of *D*, and each spark volatilizes a small portion. No loss of substance occurs, the slit of the spectroscope is protected from splashing, and the sparks are uniform, but they almost always attack the glass, causing the production of foreign spectra, such as those of calcium, lead, etc. Hartley's² apparatus (Fig. 36) is free from this drawback; the solution is poured into a U tube to one limb of which a graphite electrode is fitted, the surface having a number of deep grooves cut to facilitate the ascent of the liquid. The

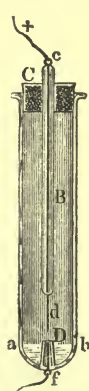


FIG. 35.

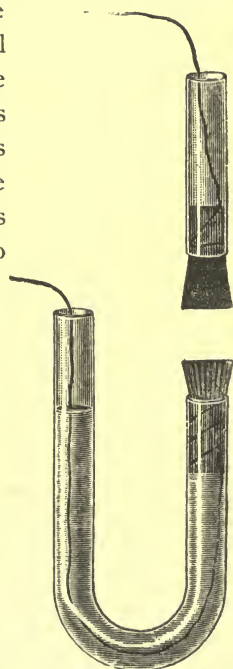


FIG. 36.

¹ C. r. (1875) 81. Journ. de Phys. de d'Almeida (1876), 5, 10.

² P. T. (1884) 175, 49, 325.

upper electrode may be either of metal or graphite, preferably the latter; both are chisel-shaped, connected with the coil by means of platinum wires, and placed exactly above one another and in a line with the slit. Other forms of apparatus designed for the same purpose have been described by Bunsen,¹ H. W. Vogel,² Lecoq de Boisbaudran,³ Salet,⁴ and Dupré.⁵

Geissler's or Plücker's Tubes.—Plücker's method⁶ is used for the investigation of gases; it consists in passing an electric discharge through rarefied gas contained in a Geissler tube (Fig. 37). The middle of the tube is usually a capillary;



FIG. 37.

platinum wires are fused through the wide closed ends, and connected inside with aluminium wires, as the passage of the current detaches particles of platinum which are gradually deposited on the glass; the light is more concentrated in the capillary, which becomes luminous, and is therefore placed in front of the slit. The tubes are filled by means of side tubes at each of the wide portions; one is connected with a mercury-pump, and the gas introduced through the other. When the operation is completed the side tubes are sealed off; this is often attended with difficulty on account of the entrance of air due to the low pressure, 1–2 mm., which is necessary in order to secure the maximum degree of brightness. Tubes intended for observation during several hours may be closed

¹ P. A. 155, 230.

² Prakt. Spectralanalyse (Berlin, 1889).

³ Spectres lumineux (Paris, 1874).

⁴ Spectroscopie (Paris, 1888).

⁵ La nature, 1882, 220.

⁶ P. A. (1859) 107, 497.

by means of stoppers accurately ground and lubricated.¹ Cornu² and Deslandes³ have given special instructions for the filling of Geissler tubes. Air is not the only impurity which is liable to be met with under extremely low pressures; the bands of carbon monoxide are frequently observed, and this is very difficult to remove. Hasselberg⁴ considers that it is only occasionally derived from the fat and rubber at the joints; it is probably liberated, together with carbon dioxide and other substances, from the glass by the electric discharge. Another disadvantage of these tubes is the thick, irregular, and non-homogeneous nature of the wall of the capillary which causes it to act as a cylindrical lens, and sometimes produces displacement of the spectrum lines. To correct this Monckhoven,⁵ Piazzzi-Smyth,⁶ Salet,⁶ Hasselberg,⁷ and others have constructed tubes with the capillary at right angles to the wide parts so that it is observed "end on." In order to obviate difficulties arising from the use of electrodes Salet⁸ has prepared tubes without them; instead the wide portions are covered with tin-foil, or, if the temperature is too high, with gold leaf; the tubes are connected with an induction-coil or with a Holtz machine, and the discharge takes place through influence; but under these circumstances the temperature in the tube is much lower than when the current is directly transmitted.

Other difficulties attend the use of Geissler tubes: the observed phenomena may be produced by minute traces of foreign bodies, and not by the gas itself; absorption by the glass and electrodes, and the extremely high temperature

¹ Hasselberg, *Mém. de l'Acad. de St. Pétersb.* (1883) [7] 31, No. 14.

² *J. d. phys. de d'Almeida* (1886) [2] 5, 100.

³ *A. c. p.* (1888) [6] 15, 28.

⁴ *Les Mondes*, 1877.

⁵ *N.* 19, 400, 458; 20, 75.

⁶ *A. c. p.* [4] 38, 52.

⁷ *Mém. de l'Acad. de St. Pétersb.* (1882) [7] 30, No. 7.

⁸ *C. r.* 73, 559.

attainable, also influence the result, but these causes are insufficient to explain many puzzling phenomena. Liveing and Dewar, and also Ames, have suggested that these are due to the discharge producing special wave-motions of the atoms, and not the pure spectrum of the substance under examination, whilst others believe that, under its influence, the molecules undergo electrolytic dissociation and the atoms are set in violent motion; it is at present impossible to give a satisfactory explanation of the matter.

Observation of the Invisible Regions of the Spectrum.

—Only the small portion of the spectrum between wave-lengths $400\mu\mu$ and $760\mu\mu$ is, in ordinary circumstances, visible to the eye, but the part beyond $800\mu\mu$ becomes perceptible if the shorter waves are cut off by means of dark-red glass, whilst those far beyond $400\mu\mu$ are seen if the longer waves are eliminated. The region beyond $760\mu\mu$ is termed the infra-red, whilst that below $400\mu\mu$ forms the ultra-violet; in the former Langley¹ reached a wave-length of $5300\mu\mu$, and Rubens² one of $5750\mu\mu$. In the ultra-violet Schumann,³ using gelatine plates, obtained photographs of a group of lines of λ $162\mu\mu$, and hydrogen lines of about $100\mu\mu$. Soret⁴ has devised a method of rendering the ULTRA-VIOLET visible by employing the fluorescence produced by the waves of short length; it consists in the introduction of a fluorescent object, such as a plate of uranium glass, into the eyepiece of a prism spectroscope. H. v. Helmholtz⁵ accomplished the same purpose by placing a thin film of quinine sulphate in the telescope at the spot where the objective forms a true image of the spectrum. Special instruments, with lenses and prisms of quartz, are required for the investigation of the ultra-violet rays, as

¹ W. A. (1884) **22**, 598. A. c. p. (1886) [6] **9**, 433.

² W. A. (1892) **45**, 238.

³ Wien. Ber. 1892. Photogr. Rundschau, 1890, 1892.

⁴ Arch. sc. phys. et nat. (1877) [2] **57**, 319; **61**, 322; **63**, 89; [3] **4**, 261; **9**, 513; **10**, 429. A. c. p. (1877) [5] **11**. C. r. (1878) **86**, 1062; **97**, 314, 572.

⁵ Optique physiologique, p. 352.

they are absorbed by glass; those of $350\mu\mu$ to a considerable extent, and those of about $300\mu\mu$ completely. Stokes¹ recommends quartz for this kind of work, but Schumann² found that it absorbs the rays below $200\mu\mu$, and was obliged to substitute it by fluor-spar; his observations on waves of shortest length, referred to above, were made with such apparatus, the spectrograph being rendered vacuous. Grating spectroscopes are specially well adapted for work with the ultra-violet if the use of glass is avoided; these rays are also absorbed by the atmosphere, which accounts for the sudden extinction of the solar spectrum at $300\mu\mu$; this is extended, Cornu³ found, with the sun at its zenith.

Photography has latterly superseded all other methods of investigating the ultra-violet rays; those below $200\mu\mu$ are absorbed by gelatine, and for such rays Schumann² employed plates without a gelatine film.

The INFRA-RED rays may be detected by their thermal and photochemical properties, and by means of phosphorescence. Their existence was first shown by William Herschel⁴ in 1800. During an investigation of the heating power of various regions of the spectrum he found that the thermometer was most affected beyond the visible red. The thermal effect was shown by Melloni⁵ to be influenced by the nature of the prism, rock salt being extremely readily transparent to long waves; later it was discovered that fluor-spar and sylvine are equally suitable, and the thermopile was used instead of a thermometer.⁶ With a grating spectroscope all absorption by the prism is avoided, but the distribution of the heat is different, the maximum being in the yellow. In place of a

¹ P. T. 1852, p. 463.

² Phot. Rundschau, 1890.

³ C. r. (1879) 88.

⁴ P. T. (1800) 90.

⁵ A. c. p. (1833) [2] 55.

⁶ Franz, P. A. (1855) 94. J. Müller, *ibid.* (1858) 105. Lamansky, *ibid.* (1872) 146. Mouton, C. r. (1879) 88; 89. Desains, *ibid.* (1880) 90; (1882) 94.

thermopile, Langley's¹ actinic balance or bolometer is employed; by its means a rise in temperature of 0.000001° C. may be detected. It consists of a Wheatstone bridge, the arms being formed of two extremely thin blackened wires of equal resistance; if the temperature of one changes, the equilibrium is disturbed and the galvanometer affected. With the aid of this instrument Langley has examined the emission-spectra of the sun and moon, and of solid bodies between 0° and 1500° , whilst flame, arc, and absorption spectra have been investigated by R. v. Helmholtz,² Julius,³ K. Ångström,⁴ Rubens,⁵ Snow,⁶ Lewis and Ferry,⁷ and Paschen.⁸

The red and infra-red rays were for long believed to be incapable of photographic action. E. Becquerel⁹ observed that the red rays affect silver chloride which has been previously exposed to light for a short time, and Draper¹⁰ succeeded in photographing the beginning of the infra-red, but complete photographs could not be produced until Abney¹¹ prepared a special bromo-silver emulsion sensitive to the infra-red. He has obtained photographs of the solar spectrum up to wave-lengths of $2700\mu\mu$, both with a prism and a grating, and has also photographed a number of absorption-spectra.

The third method of investigating the infra-red is based

¹ Sillim. Journ. [3] **21**, 187; [3] **27**, 169; (1886) [3] **31**; **32**; (1888) **36**; (1889) **38**. Proc. Amer. Acad. **16**, 342, W. A. **22**, 598.

² Die Licht- und Wärmestrahlung verbrennender Gase (Berlin, 1890).

³ Die Licht- und Wärmestrahlung verbrannter Gase (Berlin, 1890).

⁴ W. A. (1889) **36**.

⁵ W. A. **45**, 238.

⁶ W. A. (1892) **46**.

⁷ Johns Hopkins Univ. Circul. (1894) **13**, 74.

⁸ W. A. (N. F.) **50**, 409; (1894) **52**, 209.

⁹ A. c. p. (1843) [3] **9**.

¹⁰ P. M. (1843) [3] **22**.

¹¹ P. T. (1880) **171**, 653; (1886) **177**. P. R. S. (1881) **31**. P. M. [5] **3**, 22.

on E. Becquerel's¹ discovery of their phosphorescent action. A layer of Balmain's luminous paint is exposed to diffused daylight, and then to the infra-red spectrum; at first the spectrum bands become brighter, the Fraunhofer lines remaining unaltered; this soon changes and the Fraunhofer lines gain in luminosity until they appear bright on a dark ground. The results obtained in this manner by E. and H. Becquerel agree well with those of Langley and Abney.

Lommel² has improved Becquerel's method, and has prepared photographs of the infra-red with ordinary plates. The image of the spectrum is obtained in the manner described, with the Fraunhofer lines bluish and luminous; a gelatine dry plate is then laid over the image on the phosphorescent plate, and all the details are clearly reproduced. Photographs of the grating solar spectrum were made in this manner.

The grating, particularly the concave one, in combination with a prism, is especially suitable for the investigation of the infra-red, since, by means of the superposed spectra, the wavelengths in this region may be compared with those in the visible portion which are accurately known. The ordinary dispersion formula for prisms does not apply to the infra-red region.³

Observation of Absorption-spectra.—The object under examination is placed in front of the slit; if it is somewhat opaque, direct sunlight is used; the electric light, Linnemann's zirconium light, Auer's incandescent burner, a good petroleum lamp, or an ordinary Argand burner are also employed as sources of illumination. Daylight is convenient, as the Fraunhofer lines permit of ready orientation, but it is unsuit-

¹ C. r. (1866) **63**; (1873) **77**; (1876) **83**; (1887) **104**; (1888) **107**. A. c. p. (1877) [5] **10**. H. Becquerel, C. r. (1883) **96**, **97**; (1884) **99**; (1886) **102**. A. c. p. (1883) [5] **30**.

² W. A. (1883) **20**; (1887) **30**. *Sitzungsber. Münchener Akad.* (1888) **18**; (1890) **20**.

³ Langley, P. M. (1884) [5] **17**; (1886) **22**. *Sillim. Journ.* [3] **27**, 169. W. A. **22**, 598. Desains and Currie, C. r. (1880) **90**; (1882) **94**.

able for the absorption-spectra of gases, or for observations in the ultra-violet; in these cases artificial light of great brightness is necessary. If the substance under examination is a gas, it is placed in a tube with plane sides. Glass troughs with plane parallel sides are used for liquids; H. W. Vogel¹ employs ordinary test-tubes, placing them so that the light-rays pass diametrically through to the slit, and, in order to overcome the difficulty of adjustment, they are fixed in a rectangular trough of water. Gladstone² uses a wedge-shaped vessel which allows all the absorbed parts to be observed at a glance; as a substitute Landauer³ has suggested the use of the ordinary hollow prism, fixed horizontally or vertically in a stand; it permits of the rapid observation of various thicknesses of liquid, and is particularly well suited for qualitative work in which the refractive angle of the vessel may be neglected. The absorption-spectrum of a substance depends on its concentration and the thickness of the column through which the light passes; this renders its accurate characterization a matter of difficulty, and is only possible when both the above factors are given. Many observers have confined themselves to giving graphic reproductions of selected characteristic strong and faint absorptions. Krüss⁴ suggested the determination of the "minimum of brightness"; this is obtained by diluting the liquid under examination until the bands whose maxima are to be measured are readily visible; their limits are determined, and the liquid repeatedly diluted, fresh measurements being taken after each addition of water; two values are finally obtained which closely approximate if the liquid is further diluted and the minimum of brightness is situated between them.

¹ Prakt. Spectralanalyse (Berlin, 1889).

² Jour. Chem. Socy. Lond. 10, 79. P. M. [4] 24, 417.

³ Ber. (1878) 11, 1773.

⁴ *Ibid.* 16, 2051. Zeitschr. phys. Chem. 2, 312. Spezielle Methoden der Analyse (Hamburg, 1894).

Measuring Appliances and Scales.—In the last two chapters the measuring appliances have been described in detail together with the spectroscopes. Simple instruments with a prism of 60° have a millimeter scale reflected into the telescope; generally, following Bunsen's¹ suggestion, the sodium line is adjusted to the 50th division, which is also in a

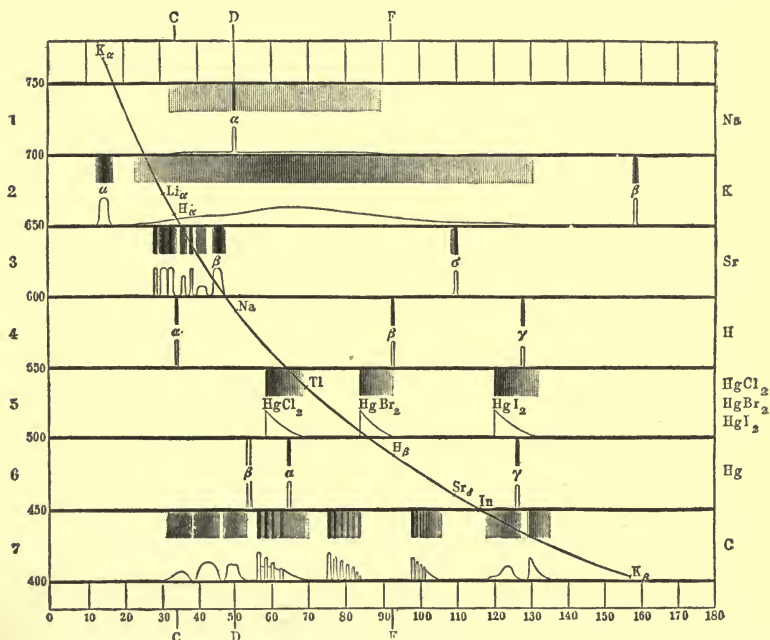


FIG. 38.

line with the fixed edge of the slit, but this is purely optional: the sodium line may be adjusted on any other division so long as the spectrum remains within the limits of the scale. Bunsen² in his earlier work had the sodium line at the 100th division, as did Lecoq de Boisbaudran³ and Krüss,⁴ whilst

¹ P. A. 119, 10.

² *Ibid.* 113, 377.

³ Spectres lumineux (Paris, 1874).

⁴ Ber. 19, 2742.

H. W. Vogel adjusts it at 0, and gives the other divisions as + or - according to their greater or less refrangibility. The divisions of the scale are usually calculated into wave-lengths, and the results given as such, since it is impossible to obtain spectroscopes of absolutely identical dispersive power. The conversion is most readily accomplished by means of an interpolation curve; the divisions of the scale are plotted as abscissæ on paper ruled into rectangular spaces, the wave-lengths from 300–800 μ form the ordinates, and the points are connected by means of a smoothly drawn curve as shown in Fig. 38, so that the interrelationship of wave-lengths and scale is seen at a glance. The table is completed by the determination of the position of the following lines as shown by the particular spectroscope employed, their wave-length is given in Ångströms (ten millionths of a millimetre), and their position on Kirchhoff and Bunsen's old scale is also added.

		Rowland's Scale. Wave-length in Ångströms.		Divisions of Kirchhoff's Scale.
Flame-spectra.	Li.....	6708.2		31.8
	Na.....	{ 5896.16 } 5890.19 }	Mean 5893.2	50.0
	Tl.....	5350.6		67.8
	Mg.....	5183.9		74.5
	Sr.....	4607.5		105.5
Fraunhofer lines.	A.....	7607.8*		17.5
	B.....	6870.2		28.9
	C.....	6563.1		35.0
	D ₁	5896.16 }		50.0
	D ₂	5890.19 }		
	E.....	5270.2*		70.9
	b ₁	5182.8		74.5
	b ₂	5172.9		74.8
	b ₃ and b ₄ ..	5168.1*		75.0
	F.....	4861.5		90.0
	G.....	4308.0*		127.3
	H.....	3968.6		161.2
	K.....	3933.8		165.7

* Mean of several lines.

Photographic scales showing wave-lengths directly may be prepared, but in certain parts the divisions are so close together that it is more convenient to use scales with equal divisions, and reduce the readings to wave-lengths. Instead of wave-lengths their reciprocals are sometimes employed, that is, the number of waves in 1 cm. at 0° in a vacuum; this value $\left(\frac{1}{\lambda}\right)$, which is termed the *oscillation frequency*, is obtained by dividing into 1 the wave-lengths reduced to 0° and a vacuum,¹ the calculation being carried to six or seven figures; some observers, including Kayser and Runge, use uncorrected wave-lengths; they justified this on the ground that the refractive index of air was not known with sufficient accuracy, and that the increase in the index, as the wave-length decreases, is so small that only a negligible error is introduced by regarding it as constant; for example, the difference between $\lambda = 6000$ and $\lambda = 2200$ is only 0.09 Ångström.²

Large instruments, with several prisms automatically adjusted to the position of minimum dispersion, have a divided circle over which the telescope travels, thus giving the measurements, whilst the micrometer-screw, which moves the last prism, is utilized for the same purpose in the case of spectroscopes in which the rays return through the prisms, since the telescope on such instruments is necessarily fixed. None of these appliances give more than approximations, since it is difficult to obtain the mechanism absolutely exact, and the refractive and dispersive power of the prisms are affected by the temperature. In order to make accurate measurements with prism instruments it is desirable to compare them with the solar spectrum, or with that of iron; both are rich in

¹ B. A. R. 1878.

² Kayser and Runge, A. B. A. 1893. Hasselberg, Öfvers. K. Vetensk. Akad. Förhandl. (1892) No. 9.

lines the wave-lengths of which have been accurately determined.

Eder¹ recommends the use of the spark-spectrum of an alloy consisting of equal parts of cadmium, zinc, and lead for the orientation of prism-spectra of medium dispersion. The most accurate ocular observations are obtained with a spectrometer fitted with a plane grating or prism, the best photographic ones with a concave grating spectroscope.

Drawings of Spectra.—The diagrammatic reproduction of spectra are made, according to Bunsen's suggestion, on paper with printed millimetre scales; the breadth of the lines and bands is given as observed in the spectroscope, and their relative brightness shown by the varying distance of the contour from the horizontal; such drawings are shown in Fig. 38,² together with the spectra as they appear in the spectroscope.

¹ Denkschr. der Wiener Akademie (1893), 60.

² From Wiedemann-Ebert, *Physikal-Practicum* (Braunschweig, 1893).

CHAPTER VI.

SPECTRA.

I. EMISSION-SPECTRA.

THREE varieties of spectra are recognized, *continuous*, *channelled* or *band*, and *line* spectra. Having described the production of spectra, and the means by which they are examined, it is necessary to consider the conditions which modify them, and also the laws governing their construction; much light has been thrown on these subjects by more recent investigations;¹ indeed spectroscopic methods appear eminently suited for the elucidation of the molecular structure of matter, since change in a spectrum indicates change in atomic motion. All substances are composed of molecules, consisting of similar or dissimilar atoms, the number of which probably varies with the temperature and pressure; the molecules are in a state of active vibration, but, in the case of solids, are maintained in proximity by their mutual attraction, the vibrations being manifested chiefly as heat. The molecules of liquids exert sufficient attraction to prevent their complete separation, but those of a gas are independent; their path through space is relatively great and their collisions comparatively few.

¹ Kayser, Spectralanalyse (Berlin, 1883). Spectralanalyse in Encyclopädie der Naturwiss. **32**. (Handb. der Physik von Winkelmann. Breslau, 1894, p. 419.) W. A. (1891) **42**. Chem. Ztg. (1892) **16**, 593. Kayser and Runge, A. B. A. 1888-1894. Rydberg, Svenska Vetensk. Akad. Handl. (1890) **23**. Deslandes, C. r. (1886) **103**, 375; (1887) **104**, 972. Julius, Ann. de l'Ecole polyt. de Delft, 1889. Wüllner, W. A. (1874) **8**; (1888) **34**. E. Wiedermann, W. A. (1878) **5**. Schuster, B. A. R. 1880. Lockyer, Studies in Spectrum Analysis (London and New York, 1878).

In addition to the motion of the molecule as a whole, there is a continuous movement of its parts; whilst the former, except for the velocity and extent of the free path, is the same for all gases, the motion of the atoms must be different for each kind of molecule, since it will be conditioned by the position, number, and mass of the atoms, by their energy, and by the nature of the collision of different molecules. The vibrations of glowing vapors, which we perceive as light, are conditioned by the vibrations of the atoms, so that change in these must produce alteration in the spectra. The nature of the relationship between the vibrations of the atoms and the luminiferous ether are unknown, but it may be assumed that the wave-motion of the latter exhibit the vibrations of the former, the number of vibrations of an observed spectral line corresponding with that of the atom itself. Maxwell showed that only the majority of the molecules of a gas are at its mean temperature, the remainder are at all possible intervals above and below this, so that the spectrum produced at a particular temperature is not pure, but a mixture, with those rays predominating which correspond with the mean temperature.

Solid bodies have their molecules closely adjacent, the atoms being restrained by external forces from producing their own vibrations, and this proximity causes the production of all possible vibrations if the collisions increase in frequency; at low temperatures the vibrations are comparatively slow and produce radiant heat; but as the temperature rises the collisions increase in violence and the vibrations in frequency, producing successively the infra-red, the red, the yellow, and so on, until, at the highest temperatures, the ultra-violet is obtained. All solids therefore exhibit continuous spectra, containing rays of every possible wave-length; the same applies to liquids, so far as they can be caused to emit spectra. The circumstances are otherwise with luminous gases and vapors: the intervals between the molecular impacts are relatively long, the characteristic individual vibrations of

the atoms are able to develop, and the corresponding waves appear in the spectrum, which is therefore discontinuous and consists of separate bright regions. Discontinuous spectra are divisible into *band* and *line* spectra, formerly termed by Plücker and Hittorf¹ spectra of the first and second order. The former usually consist of a number of bands, one edge being bright and gradually diminishing almost to darkness in the direction of the other edge; they resemble to some extent illuminated fluted columns, hence the name channelled spectra, which is also applied to them. Observed under high dispersions the channellings are resolved into numerous slender lines, arranged regularly, their proximity being greatest in the brighter regions. Band-spectra are exhibited by compounds, and also by elements at temperatures below that necessary for the production of lines.

Line-spectra consist of separate bright lines (slit images) which, if produced by means of a prism, are not perfectly vertical, but are slightly inclined towards the red; they are far less numerous than those in the band-spectra, and appear not to exhibit regularities in position and brightness. The manner in which they change into the very different band-spectra has not been explained; it is known that the latter are obtained at temperatures intermediate between those required for the production of continuous spectra and line-spectra, and it has been suggested that they are produced by molecular aggregates which would be expected to yield spectra richer in lines than those that could be formed in the presence of fewer atoms. It has long been disputed whether the chief portions of a spectrum are constant when the molecules remain the same. Wüllner² decides in the negative, and holds that, with unchanged molecules, the emission is a function of the temperature, the band-spectrum being pro-

¹ P. T. (1865) 155.

² W. A. (1879) 8; (1888) 34. Ber. Berl. Akad. (1889) 38. Comp. also his "Lehrbuch der Physik."

duced at low, and the line-spectrum at high temperatures; these together form the complete spectrum of the particular substance, and the change is continuous. The opposite view is now generally accepted, and has been chiefly developed by Kayser; according to this, so long as the molecules are unchanged their particular vibrations must remain constant, but it does not follow that at any temperature they should exhibit all their possible modes of vibration, and particularly not with equal intensity. It has been repeatedly observed that increase in the violence of impact is correlated with greater intensity in the shorter wave-lengths; the ultra-violet lines become considerably stronger if the arc is used instead of the Bunsen flame, but the longer waves also increase in brightness, lines before too faint to be seen become visible, and there is a general increase throughout the spectrum in the number and brightness of the lines. The spontaneous reversal of the lines is regarded by Kayser as a definite proof of the constancy of the spectrum within each order. Light from a luminous heated gas is absorbed by cooler gas of the same kind, but as the same rays are emitted as are absorbed by the cooler vapor it follows that the wave-length must remain unchanged, although the intensity will be considerably decreased and the original bright lines be replaced by dark ones; since such reversal occurs without alteration between all attainable limits of temperature, about 1000° – 5000° , the constancy of the emissions throughout the same range is established.

Influence of Temperature and Pressure.—It has been stated above that increase in temperature produces greater intensity in the lines within the particular order of spectrum. Increase in the pressure is accompanied by a broadening of the lines;¹ this change may be exhibited by all substances in varying degree, and it may occur symmetrically or only towards one side, in the latter case generally towards the least

¹ Comp. Schuster, B. A. R. 1880, p. 275. Roscoe and Schuster, *Spectrum Analysis* (London, 1885), pp. 136, 163.

refrangible end. The hydrogen lines may be extended to such a degree that the spectrum becomes continuous;¹ Zöllner² believed that this was due to the density of the luminous layer; his conclusion was deduced from Kirchhoff's law, but it is not in agreement with the observation that a Geissler tube exhibits the same number of sharp lines whether viewed longitudinally or transversely, and that sharp lines are shown by the solar atmosphere and prominences in spite of the enormous thickness of the former. General acceptance is now given to Lockyer and Frankland's³ view that the increase in breadth is due to greater pressure, although the temperature also exercises some influence; but, in the cases under consideration, a rise in temperature necessarily produces an increase in the pressure. The theoretical explanation of the phenomenon is as follows: so long as the molecules vibrate singly the oscillations occur regularly and at equal intervals, and therefore produce sharp lines, but if other molecules are in close proximity, the vibrations are disturbed by their impact, the frequency of which depends upon the pressure and temperature.⁴

Lockyer's Long and Short Lines.—Lockyer⁵ has devised a method which readily shows the influence of temperature and pressure on a spectrum. The arc or spark is adjusted horizontally to the vertical slit of the spectroscope, and the image thrown on to the slit by means of a lens; a spectrum is thus obtained exhibiting long and short lines of varying breadth: that shown in Fig. 39 is produced by a mixture of calcium and strontium. The image of the slit corresponds with that of a section of the arc, the middle of the image showing the lines in the middle of the arc, those at the sides

¹ Frankland, P. R. S. (1868) **16**, 416. Wüllner, P. A. (1869) **137**, 369.

² P. A. (1871) **142**, 88.

³ P. R. S. (1869) **27**, 288.

⁴ Comp. Lippich, P. A. (1870) **139**, 465.

⁵ P. T. (1873) **163**, 253, 639. Galitzin, W. A. (1895) **56**, 78.

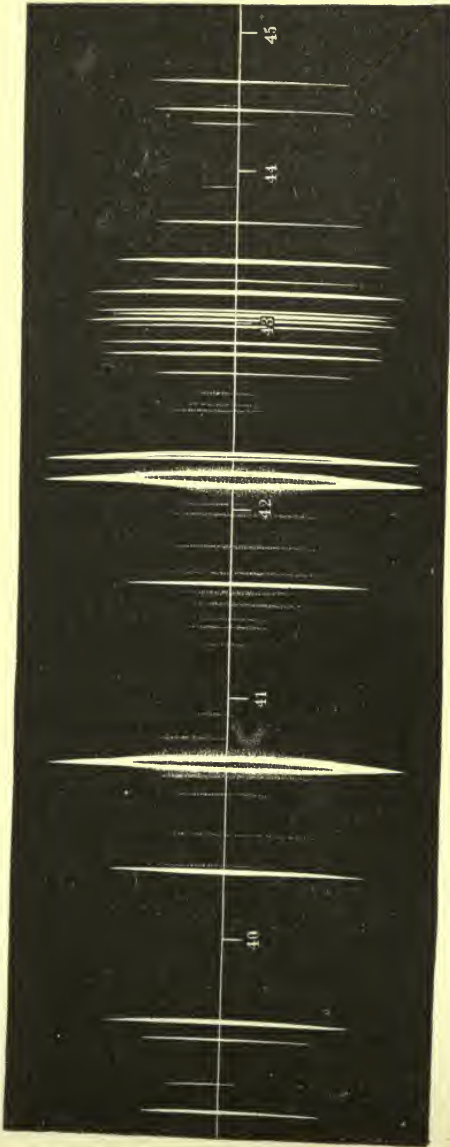


FIG. 39.

of the latter being shown at the extremities of the image. The luminous vapor is both hotter and denser in the middle than at the sides of the arc; therefore, if the spectrum is influenced by temperature and pressure, the middle of it should differ from its extremities, and this is actually the case. The longer lines are most numerous at the sides, the short ones being confined to the middle; all taper towards their extremities; moreover, the length is not dependent on the brightness of the lines, as the fainter ones may be either short or long. Lockyer considers that the longer lines are produced at lower temperatures, and correspond with the chief lines observed by the ordinary method; the short lines are due to relatively high temperatures, and the expansion in the middle is caused by the greater pressure in the interior of the arc.

Influence of Magnetic Current.—When the *D*-lines are produced by means of a Rowland's grating, and a Bunsen burner and sodium chloride, they have been observed by Zeeman¹ to widen during the passage of a current, if the burner is placed between the poles of an electromagnet. With an oxy-coal gas-flame they expanded to three or four times the normal width. Similar results were obtained with a lithium line. Interruption of the current produced an immediate reversion to the ordinary state. The widening was also observed in the absorption-lines (reversed lines) produced by sodium vapor, in a porcelain tube placed between the poles and perpendicular to a line joining them. The widening is not due to change in the density of the luminous or absorptive gases, but the observations confirm Lorentz's theory, according to which electrical phenomena are conditioned by the position and motion of electrically charged ions, by which also light vibrations are accomplished. Zeeman deduces from this theory the proposition that the broadened

¹ Zittingsverl. K. Akad. Wet. Amsterdam (1896-97), pp. 181-242. W. A. Beibl. (1897) 21, 139. Astrophys. J. (1897) 5, 332. P. M. (1897) [5] 43, 226.

spectrum-lines of a light-ray, in the direction of the magnetic current, are subjected to circular polarization, one extremity to the left, the other to the right. If the ray is at right angles to the current, both extremities are linearly polarized, at right angles to its direction.

II. ABSORPTION-SPECTRA.

Kirchhoff's Law.—Fraunhofer, in 1824, observed the coincidence of the yellow sodium lines with the double *D*-lines of the solar spectrum, and the relationship between the emission and absorption of light had been previously suggested by various workers,¹ but Kirchhoff² in 1859 enunciated and established the law which bears his name, and which is also known as the "law of exchanges." In order to directly prove the coincidence of the above lines Kirchhoff observed a moderately bright solar spectrum through a sodium flame which was placed before the slit; the dark lines were at once changed to bright ones, but with a very bright solar spectrum the lines were darker than when viewed directly. He then examined the Drummond lime-light through the sodium-flame, and got dark lines in place of the yellow ones, showing that the sodium-flame absorbs the same kind of rays that it emits. The results of these experiments, and certain theoretical considerations, led him to propound the generalization that the relationship between the emissive and absorptive power of all substances for light of the same wave-length is identical at the same temperature. The absorption-spectrum of a substance corresponds therefore with its emission-spectrum at the same temperature and in the same molecular condition. This was proved by Kirchhoff and Bunsen in the case of sodium and

¹ Ångström. P. A. (1853) 94, 141. Foucault, Bull. Soc. philom. de Paris, 1849. A. c. p. (1860) [3] 58, 476. Stokes, P. M. (1860) [4] 20, 20. Balfour Stewart, T. R. S. E. 1858.

² A. B. A. 1861, p. 64.

other volatile metals, and by Cornu,¹ Liveing and Dewar,² and Lockyer³ for others, including those that are most refractory. Kirchhoff's investigation finally proved the nature and origin of the Fraunhofer lines (comp. Chapter IX). Gases and vapors at low temperatures show absorption-spectra consisting of bands, but at higher temperatures they are composed of lines; as a rule the absorption-spectra of solids and liquids are continuous over a large portion of the field, corresponding with their continuous emission-spectra; the spectroscopic investigation of substances thus becomes possible at a temperature below that at which they are luminous.

Kirchhoff's law indicates that the luminosity of bodies is due to increase in their temperature. Objection has been made to this by more recent investigators; thus E. Wiedemann⁴ has shown that, apart from the normal evolution of light, causes other than rise in temperature may produce luminosity in a body, and to this *luminescence* he considers that Kirchhoff's law does not apply. Hittorf⁵ and W. v. Siemens⁶ have also shown that, up to a temperature of about 2000°, gases emit no light, whilst Pringsheim⁷ believes that vapors cannot become luminous by increase of temperature alone, but only in consequence of undergoing chemical change. At present it is not possible to say how far these objections are justified; even if correct they do not necessarily invalidate the law of exchanges, which has received support from the theory of resonators. The mechanism of light absorption is as yet far from being completely understood.

Influence of Temperature and Physical State.—Absorption-spectra are usually observed at low temperatures, thus

¹ C. r. (1871) **73**, 332.

² P. R. S. **28**.

³ Studies in Spectrum Analysis (London and New York, 1878).

⁴ W. A. (1888) **34**, 446.

⁵ *Ibid.* (1879) **7**; (1883) **19**.

⁶ *Ibid.* (1883) **18**.

⁷ *Ibid.* (1892) **45**.

readily permitting the determination of the influence of the molecular constitution. The absorption-spectra of iodine in the solid form, in solution, and in the gaseous state are all different; indeed in the latter state it exhibits a line and a band spectrum corresponding with its two emission-spectra. A rise in temperature causes an increase in the absorption within the same order of spectra.

H. W. Vogel¹ found that if solutions of organic dyes are volatilized on glass plates, the residue usually exhibits a different spectrum from that of the solution, but the latter remains unchanged if gelatine, glue, starch, or gum arabic is added to the solutions before drying. Stenger² states that in the gelatine film the molecular aggregation is the same as in solution, hence the identity of spectrum; in its ordinary solid state the dye is composed of more complex molecules and therefore has a different absorption-spectrum.

Influence of the Solvent.—Solutions of substances which exhibit absorption-spectra consisting of bands frequently show no regularity in the changes which occur when other solvents are employed. In this connection Kundt³ has propounded the following rule, which, however, is not of universal application: comparing two colorless solvents which differ considerably in refractive and dispersive power, the one in which these are greater will cause the absorption-bands to approach the red end of the spectrum. Stenger⁴ accounts for the exceptions to the above rule by suggesting that the spectrum of a substance is dependent both on its chemical composition and on its molecular state; if the physical molecules in the solution are identical with the chemical ones, the body follows Kundt's rule, but solutions frequently contain aggregates composed of a number of chemical molecules.

¹ Ber. Berl. Akad. 1878, p. 409.

² W. A. (1888) 33, 583.

³ P. A. Jubelband (1874) p. 615. W. A. (1878) 4, 34.

⁴ W. A. (1888) 33, 577.

The deviation from, or agreement with the rule may also be due to the varying extent to which the substance in solution undergoes electrolytic dissociation.

Influence of Optical Density.¹—The influence of concentration and of the thickness of the layer of substance has been already considered in the preceding chapter. The experiments of Bunsen and Roscoe² show (1) that the quantity of light absorbed by a layer of infinite thickness is proportional to the quantity (intensity) of the incident-rays. (2) The quantity of light absorbed is dependent on the density of the absorbent. The *coefficient of absorption*, calculated from these data, gives the relationship in intensity between the incident and emergent rays for a layer of unit thickness; in place of this, Bunsen and Roscoe employ the *coefficient of extinction*, which facilitates the calculation of the concentration from the absorption; the term is applied to the reciprocal of the thickness of substance required to reduce the light to one tenth of its original intensity.

Fluorescence and Absorption.—Absorption of light is connected with phosphorescence and fluorescence. Certain substances become luminous by the action of light; if the luminosity ceases on the withdrawal of the light, they are said to be fluorescent, whilst the term phosphorescent is applied to substances which continue to be luminous after the light is cut off. Hitherto fluorescence has only been observed in the case of liquids, and phosphorescence in that of solids. In accordance with the law of the conservation of energy, the rays causing these phenomena are absorbed; fluorescent bodies exhibit corresponding absorption-spectra, and, as they absorb the ultra-violet rays more or less completely, they all fluoresce in this region of the spectrum.

¹ Comp. O. Knoblauch, W. A. (1891) 43, 738.

² P. A. (1857) 101, 235.

III. RELATIONSHIP BETWEEN THE LINES OF AN ELEMENT.

Observation of different elements shows that some have lines distributed throughout the whole spectrum field, whilst others exhibit only a few single lines or groups, so regularly arranged as to suggest the idea of a definite relationship. Early investigations led to the conclusion that an acoustical law could be applied to the luminiferous vibrations of the molecules; a string vibrating as a whole gives a fundamental note, but if it vibrates in parts the number of vibrations in the notes produced is 2, 3, 4, etc., times that of the fundamental note; if this law applies in optics, the wave-length of the different lines of a spectrum must bear a mutual ratio represented by whole numbers.

The first attempt to discover such regularities was made by Lecoq de Boisbaudran¹ in the case of the nitrogen lines; his conclusions were based on wave-length determinations of insufficient accuracy, and were not confirmed by Thalén. Stoney² was more successful, and showed that the ratio of the hydrogen lines $C : F : h = 20 : 27 : 32$; the subject was further investigated by Stoney and Reynolds,³ Soret,⁴ and others, until the more thorough work of Schuster⁵ rendered the theory no longer tenable. He showed that, even when there is absolutely no connection between the lines, the chances are in favor of a harmonic relationship in spectra rich in lines, and, whilst many facts indicate the existence of a mutual relationship between the wave-lengths, the law which it follows is as yet undiscovered. The subject ceased to attract attention for several years until Balmer⁶ published a formula which reproduces with wonderful accuracy the posi-

¹ C. r. (1869) **69**, 694.

² P. M. (1871) [4] **41**, 291.

³ *Ibid.* (1871) [4] **42**, 41.

⁴ *Ibid.* [4] **42**, 464.

⁵ B. A. R. 1880. P. R. S. (1881) **31**, 337.

⁶ W. A. (1885) **25**, 80.

tion of the hydrogen lines. The values are given by the expression

$$\lambda = A \frac{n^2}{n^2 - 4}.$$

n is a whole number between 3 and 15, A a constant, 3645.42 Ångströms according to Cornu's measurements, or 3647.20 taking Ames' more accurate determinations; the possible error in the latter is only 0.1–0.3 Ångströms, and the agreement between the observed wave-lengths and those calculated from the above formula is within these limits. Cornu,¹ simultaneously with Balmer, pointed out that the wave-length of the readily reversible lines of aluminium and thallium bear a definite relation to those of hydrogen, whilst a few years later Deslandres² gave a formula for the lines composing the bands of numerous elements.

In 1887 Kayser and Runge³ commenced their investigations, and succeeded in obtaining a formula which reproduces "series" in the case of a considerable number of elements; Balmer's formula for the hydrogen lines is only a special instance of their more generalized expression. The term "series" is applied to related lines, which are particularly numerous in the spectra of the metals of the alkalis and alkaline earths. Attention had been called to these by Living and Dewar⁴ before the publication of Balmer's work. The distance between two consecutive lines decreases with diminishing wave-length, so that the lines asymptotically approach a limit; they applied the term "harmonic" to such a series of similar groups.⁵ Taking the refractive index of air as con-

¹ C. r. (1885) 100, 1181.

² *Ibid.* (1886) 103, 375; (1887) 104, 972.

³ Ueber die Spectren der Elemente A. B. A. 1888, 1889, 1890, 1891, 1892, 1893. W. A. (1894) 52, 114. Runge, B. A. R. 1888, p. 576. Kayser, Chem. Ztg. (1892) 16, 533. Encyklopädie der Naturw. 32 (Winkelmann's Handb. der Physik. Breslau, 1894) p. 429.

⁴ P. T. 1883, p. 213, and also previously.

⁵ *Ibid.* 1884.

stant, a value proportional to the number of waves, i.e., the reciprocal, was used by Kayser and Runge in place of the wave-length; thus modified Balmer's formula becomes

$$\frac{1}{\lambda} = A + Bn^{-2}, \text{ and then } \frac{1}{\lambda} = A + Bn^{-2} + Cn^{-4}.$$

This expression gives only an approximation; probably the number of waves is only a function of n which, in the negative power, admits of the development of a rapidly convergent series; of these the first three terms are sufficient to give their values with remarkable accuracy. Kayser and Runge then extended their investigations so as to elucidate the following questions: the applicability of the formulæ in the case of measurements of the highest possible degree of accuracy; whether lines of wave-lengths indicated by the formulæ really exist; can all the lines of every element be reduced to series? can a relationship be shown between the constants of the formulæ of different elements?

The investigators' objects could not be attained by the use of the older wave-length measurements, partly on account of their inaccuracy, partly because they did not include the ultra-violet, so that it became necessary to re-examine the spectra of the elements with the highest possible degree of accuracy. The largest number of series represented by the above formulæ are exhibited by the spectra of the members of Mendeléeff's first three groups. The metals sodium, potassium, rubidium, cæsium, copper, silver, aluminium, indium, and thallium each have two series in which B and C are identical and A differs; two such series may therefore be regarded as a series of pairs of lines, each pair having the same difference in vibration. Probably all elements have two such series of pairs. The first series contains strong, ill-defined lines, and is termed the first "subseries"; the second series contains well-defined fainter lines, sometimes broaden-

ing out towards the red: they form the second subseries. The two subseries were not observed in the spectra of rubidium and cæsium; lithium exhibits both series, but they consist of single lines instead of pairs. The difference in wave in both series is practically identical in the case of each element, and bears a relationship to its atomic weight. The alkali metals have a third series which includes the strongest and most readily reversible lines of the whole spectrum, and is called the "principal series"; in the spectrum of lithium it consists of single lines, in the other metals of pairs; these are closely adjacent in the case of sodium, but with increasing atomic weight the separation becomes greater, whilst the entire series gradually approaches the least refrangible portion of the spectrum. In each pair the stronger line has the smaller wave-length; this was already known to be true of the sodium *D*-lines. Within each principal series the difference in the number of waves between the pairs is approximately inversely proportional to the fourth power of the ordinal number. The largest positive value given by the formulæ for all series hitherto observed corresponds with the ordinal number 3; the lines where $n = 3$ are comparable with fundamental notes, since they represent the longest possible waves, exactly as exhibited in Balmer's formula for the hydrogen lines.

The spectra of copper, silver, and gold do not show such striking regularities as those of the alkali metals, which appear all to be arranged on one plan. By analogy with the order observed in other spectra the existence in the spectra of copper and silver of both subseries of pairs can be demonstrated; but this is not so with gold, possibly because the series become fainter as the atomic weight increases.

Magnesium, calcium, and strontium, amongst the alkaline earths, have spectra with two subseries consisting, not of pairs, but of triplets with a constant difference of wave: as the atomic weight increases the series diminish in intensity and approach the red end of the spectrum. This probably ex-

plains why no series could be found in the case of barium, the last element in this group.

The spectra of zinc, cadmium, and mercury also exhibit two subseries of triplets, but scarcely half the total number of lines is included in the series.

Only a few of the elements in Mendeléeff's fourth and fifth groups have been available for Kayser and Runge's investigations, which have been confined to tin and lead in the former, and to arsenic, antimony, and bismuth in the latter; the regularities found in the members of the first three groups could not be detected in these. Each spectrum is characterized by a large group of lines which are repeated in such a way that, by the introduction of a constant, the number of waves of one group may be deduced from that of another, but the lines do not permit of arrangement into series, and their appearance gives no clue as to their possible interrelationship. It is not surprising that all the lines of a spectrum do not fall into series, for in order to compare different elements they should be investigated under the same relative conditions, and not at the same temperature. Failing accurate knowledge of the temperatures at which the elements would be in a uniform molecular condition, it may be assumed that those of high melting and boiling point would require a much hotter flame than the more volatile ones; consequently if an arc lamp, giving a temperature of 3000° – 3500° , is required in order to produce the complete series in the case of the readily fusible alkali metals, it follows that, with the other elements, the higher the melting-point the less characteristic will the series be.

Working independently of Kayser and Runge, Rydberg¹ simultaneously adopted the same view of the structure of

¹ C. r. (1890) 110, 394. Zeitschr. physikal. Chem. (1890) 5, 227. Svenska Vetenskap. Akad. Handlingar Stockholm (1890), 23, No. 11. W. A. (1893) 50, 629; (1894) 52, 119.

line-spectra; he employed the number of waves instead of the wave-length, and his investigations of the members of the first three groups of the periodic system led him to conclude that the "long" lines form pairs or triplets which, in the case of each element, are characterized by a constant difference (v) in the number of waves of the components. In each group of elements this value increases in a ratio somewhat exceeding the square of the atomic weight. The triplets occur in the first and third groups, the valency of which is odd; the components of the double lines form series, the members being functions of consecutive whole numbers; each series can be approximately reproduced by the expression

$$n = n_0 - \frac{N_0}{(m + \mu)^2},$$

where n is the number of waves, m any whole number, the ordinal number of the member, and $N_0 = 109721.6$, a constant applicable to all the series of every element, and which is obtained from Balmer's formula; n_0 and μ are constants peculiar to each series, n_0 being the limit which the number of waves n approaches if m is infinite. Like Kayser and Runge, Rydberg distinguishes three kinds of series, "*nebulous*," "*sharp*," and "*principal*"; the first two are composed of pairs or triplets, so that the elements of the first and third groups have four different series of these two kinds, and the elements of the second group have six; they are termed the first, second, and third nebulous or sharp series; the lines of the first series of either kind are the strongest and least refractive. In the case of the elements in group one, the principal series contains the strongest lines of the spectrum, the nebulous series are next in order, and the sharp series the faintest; in both the separate groups and series the intensity of the light decreases as the ordinal number rises.

The different series of an element are sufficiently related

to show that they all belong to one system of waves; the series of the same group, nebulous or sharp, have the same value for μ ; the difference of the n_0 value is equal to v or v_1 and v_2 ; the series of the same order, first, second, or third, have the same value for n_0 in the different groups, but differ in that for μ . The wave-length and the corresponding number of waves, the values of the constants v , n_0 , and μ of the corresponding series in the various elements, are periodic functions of the atomic weight; the periodic difference in the constants permits of the calculation of the spectrum of an element if the spectra of the elements adjacent to it in the periodic system are known.

Rydberg's investigations have strengthened the arguments in favor of a single system of waves, and indicate the possibility of representing all the lines of a spectrum by a single formula, but they are opposed to the idea of a mixed spectrum such as would be produced by molecules at varying temperatures. He considers it probable that each element possesses only a single spectrum, and that the intensity of the series and of the special lines varies with the temperature and density of the luminous gas, in a manner similar to the changes in the overtones of a bell. The arrangement of band-spectra suggests, even more strongly than line-spectra, the possibility of their structure conforming to definite rules; Lecoq de Boisbaudran¹ and Thalén² pointed out certain regularities, but these did not permit of the deduction of a law which was first formulated by Deslandres.³ The lines of a band form series of similar lines, the series being connected in such a manner that, in each one, the distances between two consecutive lines are approximately in arithmetical progression. If the edge of a band is designated by 0 and the follow-

¹ C. r. (1869) 69.

² Svenska. Vetensk. Akad. Handl. (1869) 8.

³ C. r. (1886) 103, 375; (1887) 104, 972. A. c. p. (1888) [6] 15. J. de Phys. (1890) [2] 10, 276.

ing lines by the succeeding numbers 1, 2, 3, . . . n , then the number of waves of the n th line is given by the formula

$$\frac{1}{\lambda_n} = a + b_n^2,$$

where a is the number of waves of the edge, and b the difference between this and the number of waves of the first line. The different bands of a spectrum are related in such a manner that the first, second, etc., edges of all are represented by the expression

$$\frac{1}{\lambda} = A + B + C_n^2,$$

corresponding with that representing the lines of a series; A , B , and C are constants, and n progressive numbers. The absolute validity of these laws is questioned by Kayser and Runge,¹ but maintained by Deslandres. Theoretical articles on the origin of lines, pairs, etc., have been published by Lecoq de Boisbaudran,² Stoney,³ Julius,⁴ and v. Kövesligethy.*

IV. RELATIONSHIP BETWEEN THE SPECTRA OF DIFFERENT ELEMENTS.

Attention was first directed to this subject by Lecoq de Boisbaudran⁶ in 1869; he pointed out the similarities in the structure of the spectra of potassium, rubidium, and cæsium, and, applying the term "homologous" to certain analogous lines in each, he concluded that in the case of the metals of the alkalis and alkaline earths the spectra approximate the red as the atomic weight increases. This has been confirmed

¹ A. B. A. 1889.

² C. r. (1869) 69, 445, 606, 657.

³ P. M. (1871) [4] 41. Trans. Dubl. Soc. (1891) [2] 4. P. M. (1892) [5] 33.

⁴ Ann. de l'école polyt. de Delft (1889), 5.

⁵ Theor. Spectralanalyse (Halle, 1890).

⁶ C. r. (1869) 69, 610.

by later and more exact measurements. He¹ subsequently employed these homologous lines for the calculation of the atomic weights of gallium and germanium, which had not then been determined; his method was based upon the rule which he had enunciated, that within the groups of the periodic system the variation in the increase of the atomic weight is proportional to that of the increase in the wave-length of the homologous lines. The following is an example of the method of calculation:

	Atomic Weight.	Difference.	Difference.	Variation.	Mean Wave-length of Two Lines.	Diff.	Variation.
Si..	28.0				4010		
Ge..	"	90.0			4453	443	
		Between Si and Sn					$\frac{40.51}{100}$
Sn..	118.0				5077	624	
Al..	27.5	42.4			3952	149	
Ga..	69.9		1.2	$\frac{1.2}{42.4} = \frac{2.8302}{100}$	4101	205	$\frac{37.584}{100}$
In..	113.5	43.6			4306		

The fraction $\frac{2.8302}{100}$ means that in order to obtain 43.6, 2.8302 per cent of the difference 42.4 must be added; the variation (x) for the group Si, Ge, Sn is obtained from the ratio $37.584 : 2.8302 :: 40.51 : x = 3.051$ per cent; the increase (y) in atomic weight from Si to Ge = $\frac{90}{2.03051} = 44.32$, and therefore the atomic weight (n) of germanium = 72.32. Kayser² considers that, whilst the above rule perhaps contains a nucleus of truth, it is at present not applicable, and requires a knowledge of atomic weights considerably exceeding in accuracy almost all the current values. In consequence of this Ames³ was unable to apply the rule to magnesium, zinc,

¹ C. r. 86, 943; (1886) 102, 1291. Ber. 19, 479c.

² Spectralanalyse, in Encyclopädie der Naturw. 32 (Winkelmann, Physik. Breslau, 1894) p. 440.

³ P. M. (1890) [5] 30.

and cadmium, although his fundamental homologous lines were correctly selected; since the selection of homologous lines is to some extent arbitrary, the close agreement in the calculated values for gallium and germanium must have been partly due to chance. Ditte,¹ Troost and Hautefeuille,² Ciamician,³ Hartley,⁴ Ames,⁵ and Grünwald⁶ have also investigated the interrelationship of the spectra of various elements, but Ames' work alone has proved to be of permanent value. He measured the wave-length of the triplets in the spectra of zinc and cadmium, and calculated the differences in the number of waves between the third lines of the triplets; they decrease from triplet to triplet, are nearly identical for each element, and prove the lines to be true homologues. In the more strongly nebulous series the values for zinc are 581, 263, 141, 84, and for cadmium 587, 264, and 84.

The investigations of Kayser and Runge, and of Rydberg have thrown most light on the relation between the spectra of different elements. Their method consists in a combination of calculation and observation, their own exact remeasurements of spectrum-lines being utilized by the first two observers. The relationship of the spectra of different elements follows from the law already stated which expresses the connection between the lines of a single element. In spectra of similar structure the homologous lines are those with identical ordinal numbers. The work hitherto completed shows that the spectra fall into the same groups as the elements. In the case of the first three groups of the periodic

¹ C. r. (1871) **72**, 620.

² *Ibid.*

³ Wien. Ber. (1878) **78**, 767; (1880) **82** [2].

⁴ Jour. Chem. Soc. London (1882) 84; 1883, 390.

⁵ P. M. (1890) [5] **30**, 33.

⁶ Astr. Nachr. (1887) **117**. Wien. Ber. (1887) **96** [2]; (1889) **97** [2]; (1890) **98** [2]. Wien. Anz. 1890. Comp. also Ames, N. (1888) **38**. Kayser, Chem. Ztg. (1889) **13**; (1890) **14**. Runge, P. M. (1890) [5] **30**. Grünwald, Chem. Ztg. (1890) **14**.

system the subdivisions are also well marked, so that the following classification may be made:

1. Lithium, sodium, potassium, rubidium, cæsium.
2. Copper, silver.
3. Magnesium, calcium, strontium.
4. Zinc, cadmium, mercury.
5. Aluminium, indium, thallium.

In each of the above groups the spectrum approaches the red as the atomic weight increases, but in passing from group to group it approximates towards the violet. The systematic representation of these spectra as given by Kayser and Runge is shown in Fig. 40; the values given are the number of vibrations, and, for the sake of clearness, only the first lines of pairs and triplets which have been actually observed are shown; the figures opposite to the lines are their ordinal numbers.

The interrelationship of spectra and atomic weights has been already referred to; it may be briefly expressed by saying that the breadth of pairs and triplets, measured by the difference in the number of their waves, is approximately proportional to the square of the atomic weight.

CHAPTER VII.

SPECTRA OF THE ELEMENTS.

AN accurate knowledge of spectra is of the greatest importance for any application of spectrum analysis; the standard of measurement is the wave-length in air, at medium temperatures, under a pressure of 760 mm. expressed in Ångström's units (Å) or tenths ($\mu\mu$). Until recently all observations were based on Ångström's wave-length determinations, and on his drawings of the solar spectrum (Spectra normal du Soleil¹); this scale was universally employed during twenty years, but after Ångström's death it was shown by Thalén² to be inaccurate in consequence of Ångström having used a reputed metre measuring-rod less than one metre in length. New determinations of absolute wave-lengths have been subsequently made by Müller and Kempf,³ Kurlbaum,⁴ Peirce,⁵ and Bell;⁶ of these the values for the D_1 -line of Peirce and of Bell agree exactly, and that of Müller and Kempf very closely; the latter is used as the basis of the Potsdam system. Since the relative values are often of greater importance for spectroscopic purposes than the absolute ones, Rowland⁷ combined the various numbers as shown below, and employed the mean value as the foundation of his

¹ Recherches sur le spectre du soleil (Upsala, 1868).

² Sur le spectre de fer. N. A. S. U. 1884 [3].

³ Publicat. des Astrophysikal. Obs. zu Potsdam (1886), 5.

⁴ W. A. (1888) 33, 159, 381.

⁵ Sillim. Journ. [3] 18, 51.

⁶ P. M. (1888) [5] 25, 245, 350.

⁷ Astronomy and Astrophysics (1893), 12, 321. P. M. (1894) [5] 36, 49.

A list of the standard wave-lengths is given in the chapter on the solar spectrum together with references to Rowland's latest publications on the subject.

solar atlas, and standard wave-lengths obtained by the coincidence method; as this admits of a degree of exactitude (0.01\AA) otherwise unattainable, all recent measurements have been based on his scale.

Relative Weights.	Observer.	D_1 .
1	Ångström, corrected by Thalén	5895.81
2	Müller and Kempf.....	5896.25
2	Kurlbaum.....	5895.90
5	Peirce.....	5896.20
10	Bell.....	5896.20
	Mean.....	5896.156

The wave-lengths of the spectrum lines given in the succeeding pages are all based on Rowland's system; this has entailed a recalculation, by the use of Watts' tables,¹ of all measurements published before 1889, and also of certain others. The object of the tables was to exhibit the relationship between Ångström's and Cornu's solar atlases and Rowland's. To reduce Ångström's scale to his own system of wave-lengths Rowland multiplies the values by the factor 1.00016.

Such recalculations are open to objections, but these are overruled by the great inconvenience of wave-lengths determined by two different scales, particularly when they refer to the same element; moreover the table permits of the revised values being reconverted into the original ones. The accuracy of the older measurements should not be overrated, it falls far short of that attainable by the use of the grating and photographic appliances, such as have been used by Kayser and Runge, Liveing and Dewar, Hartley and Adeney, Hasselberg, Ames, Trowbridge, and others. Most of the older measurements, with the references, have been taken from Watts' "Index of Spectra,"²

¹ B. A. R. (1890). (London, 1891), p. 224.

² Manchester, 1889. Continuations are given in the B. A. R.

TABLE FOR THE REDUCTION OF ÅNGSTRÖM'S AND CORNU'S WAVE-LENGTHS
TO ROWLAND'S VALUES, DERIVED FROM THE UNIT $D_1 = 5896.156$.

Wave-length.	Corr.	Wave-length.	Corr.
Above 6930	+ 1.7	From 4970 to 4935	+ 1.0
From 6930 to 6880	1.6	" 4935 " 4865	0.9
" 6880 " 6820	1.5	" 4865 " 4740	1.0
" 6820 " 6800	1.4	" 4740 " 4650	0.9
" 6800 " 6765	1.3	" 4650 " 4470	0.8
" 6765 " 6720	1.2	" 4470 " 4380	0.7
" 6720 " 6660	1.1	" 4380 " 4170	0.6
" 6660 " 6230	1.0	" 4170 " 4130	0.7
" 6230 " 6180	0.9	" 4130 " 4100	0.8
" 6180 " 6155	1.0	" 4100 " 4060	0.7
" 6155 " 6135	1.1	" 4060 " 4040	0.6
" 6135 " 6130	1.0	" 4040 " 3850	0.7
" 6130 " 6110	0.9	" 3850 " 3730	0.6
" 6110 " 6080	1.0	" 3730 " 3720	0.5
" 6080 " 6060	1.1	" 3720 " 3660	0.4
" 6060 " 6000	1.0	" 3660 " 3640	0.8
" 6000 " 5970	0.9	" 3640 " 3620	0.6
" 5970 " 5810	1.0	" 3620 " 3530	0.8
" 5810 " 5780	0.9	" 3530 " 3480	0.6
" 5780 " 5610	1.0	" 3480 " 3470	0.8
" 5610 " 5540	1.1	" 3470 " 3440	0.7
" 5540 " 5485	1.0	" 3440 " 3420	1.1
" 5485 " 5435	0.9	" 3420 " 3360	1.7
" 5435 " 5350	1.0	" 3360 " 3330	2.5
" 5350 " 5335	0.9	" 3330 " 3290	2.2
" 5335 " 5325	1.0	" 3290 " 3280	2.0
" 5325 " 5300	0.9	" 3280 " 3240	1.9
" 5300 " 5175	1.0	" 3240 " 3220	1.8
" 5175 " 5150	0.9	" 3220 " 3190	0.8
" 5150 " 4990	0.8	" 3190 " 3160	0.4
" 4990 " 4970	0.9		

which gives a fairly complete list of the measurements of line-spectra made before its appearance. In the following pages the lines of each spectrum or portion of a spectrum are all from one series of measurements, and that the newest or most trustworthy; only the brighter lines have been included.

in general those between 1 and 3 on the German scale of brightness, in which the brightest is 1 and the faintest 6. In the English scale the brightness increases from 1 to 10, so that the lines included are those between 6 and 10, but where the fainter lines are characteristic they have also been given. The lines are not provided with intensity-scale numbers which are only of value in the case of closely adjacent lines, whilst their assignment is always somewhat arbitrary, but in order to facilitate orientation the specially bright lines have been printed in bolder type. The arrangement of the tables follows the ordinary plan: double or triple lines are enclosed in parentheses; bands are indicated by *b*, those sharply bounded at the red end and shading gradually towards the violet are distinguished by *b'*, those showing the opposite behavior by *b''*. Lines which are usually designated by a number or letter, such as the D_1 -line, have these enclosed in brackets, and prefixed to the wave-length; measurements are given to as many places of decimals as are required by the accuracy of the observation. Listing's¹ scale is used for the classification of the lines according to color; it runs as follows:

.... to 7230 infra-red.	5850 to 5750 yellow.	4540 to 4240 indigo.
7230 " 6470 red.	5750 " 4920 green.	4240 " 3970 violet.
6470 " 5850 orange.	4920 " 4550 blue.	3970 "ultra-violet.

The *delicacy* of spectrum reactions has been determined by Kirchhoff and Bunsen for certain flame-spectra, and by Cappel for a series of spark-spectra; the number in the table below gives that fraction of a milligram of pure substance that could be detected.

KIRCHHOFF AND BUNSEN.²

Barium chlorate.....	1000	Potassium chlorate.....	1000
Cæsium chloride.....	20000	Rubidium chloride.....	5000
Calcium chloride.....	16666	Sodium chlorate.....	3000000
Lithium chlorate.....	IIIIII	Strontium chloride.....	16666

¹ P. A. (1868) 131, 564.² *Ibid.* (1860) 110, 161.

Cappel's¹ results are as follows:

Barium.....	900000	Gold.....	4000	Nickel.....	600
Bismuth....	70000	Indium.....	90000	Potassium..	400
Cadmium...	18000	Iron.....	26000	Rubidium..	1000
Cæsium....	4000	Lead.....	20000	Silver.....	12000
Calcium....	10000000	Lithium....	40000000	Strontium..	100000000
Chromium..	4000000	Magnesium.	500000	Thallium...	80000000
Cobalt.....	15000	Manganese.	200000	Tin.....	17000
Copper.....	20000	Mercury...	10000	Zinc.....	600000

ALUMINIUM.

The visible portion of the spark-spectrum of aluminium has been investigated by Kirchhoff,² Thalén,³ and Lecoq de Boisbaudran,⁴ and the ultra-violet region by Hartley and Adeney, and Cornu;⁵ the latter gave a graphic representation of the lines of shortest wave-length, together with a formula from which Julius⁶ was enabled to calculate the wave-length. The arc-spectrum has been measured by Liveing and Dewar,⁷ and more recently by Kayser and Runge,⁸ who were unable to detect a single line in the visible spectrum, although the bands of alumina were always visible. These have been investigated by Hasselberg, and are given in a separate table below.

Arc and spark spectra:

5723.5*	5696.5*	5057.4*	4662.9*	3961.68	3944.26	3092.95
3092.84	3082.27	3066.28	3064.42	3060.04	3057.26	3054.81
3056.19	2660.49	2652.56	2575.20	2568.08	2378.52	2373.23
2367.16	2269.20	2263.52	2210.15	2204.73	2174.13	2168.87
2150.69	2145.48	1989.90	1935.25	1862.20	1854.09	

¹ P. A. (1870) **139**, 628.

² A. B. A. 1861.

³ N. A. S. U. (1868) [3] **6**.

⁴ Spectres lumineux (Paris, 1874).

⁵ Spectre normal du Soleil (Paris, 1881). C. r. (1885) **100**, 1181.

⁶ Naturk. Verh. d. Akad. v. Wetensch. Amsterdam (1888), **26**.

⁷ P. R. S. **28**, 367. P. T. (1883) **174**, 220.

⁸ A. B. A. 1892. Runge, W. A. (1895) **55**, 44. See also E. Becquerel, C. r. **96**, 1218; **97**, 72.

* Visible only in the spark spectrum. (Thalén.)

ALUMINIUM OXIDE.¹

Arc-spectrum:

Group 5210—5079:

5162.05	5156.45	5155.42	5147.93	5143.27	5143.08	5123.79
(5123.57)	5123.47)	5102.84	5102.32	5079.52		

Group 5041—4842:

4914.35	4909.55	4908.21	4906.71	4906.52	4906.07	4905.22
4905.04	4904.84	4903.72	4903.54	4899.16	4895.20	4895.00
4892.32	4890.44	4888.57	4888.41	4887.79	4886.08	4885.87
4883.45	4882.43	4882.24	4881.25	4880.07	4879.91	4878.90
4878.79	4877.75	4876.64	4876.56	4875.46	4873.50	4873.35
4872.46	4872.29	4871.48	4870.46	4869.45	4868.42	4867.48
4866.54	4863.09	4862.77	4842.44			

Group 4842—4648:

4810.16	4809.80	4766.75	4766.53	4760.32	4752.53	4752.27
4749.19	(4745.17)	4744.95)	4742.56	(4736.08)	4735.94)	4727.40
(4719.41)	4719.29)	4715.45	4711.98	4711.81	(4707.53)	4707.26)
(4706.26)	4706.17)	(4706.01)	4705.89)	4699.00	4697.90	(4695.30)
4694.78)	4689.77	4672.15	4658.68	4655.34	4648.14	

Group 4648—4471.

4593.97	4570.44	4557.84	4547.33	4543.23	4537.69	4534.24
(4523.45)	4522.86)	4516.54	4511.38	4494.22	4478.64	4470.63

ANTIMONY.

The spark-spectrum is obtained either by the use of the metal or of a concentrated solution of the chloride; it has been measured by Kirchhoff,² Huggins,³ Thalén,⁴ and Hartley and Adeney.⁵ The arc-spectrum, which differs from that of the spark, has been investigated by Liveing and Dewar,⁶ and the portion commencing at $\lambda = 643\mu\mu$ by Kayser and Runge.⁷

¹ Hasselberg, K. Svenska Vetensk. Akad. Handl. (1892) **24**, No. 15. Lecoq de Boisbaudran. Spectres lumineux (Paris, 1874). Thalén, Upsal. Universit. Arsskrift. 1866. Lockyer, P. T. **163**, 658.

² A. B. A. 1861.

³ P. T. (1864) **154**, 139.

⁴ N. A. S. U. (1868) [3] **6**.

⁵ P. T. (1884) **175**, 126.

⁶ *Ibid.* (1883) **174**, 221.

⁷ A. B. A. 1893. Also Lockyer, P. T. (1873) **163**, 369. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874).

In the visible portion of the field the lines are feeble and ill-defined, and are not present in the spark-spectrum, the lines of which are absent from the arc-spectrum. According to Lockyer and Roberts¹ antimony vapor produces a continuous absorption-spectrum in the blue.

Arc and spark spectra:

6302.8*	6129.7*	6079.2*	6004.7*	5910.1*	5894.6*	5639.1*
5568.25	4949.7*	4878.6*	4592.4*	4352.6*	4265.6*	3739.6†
3598.6†	3566.8†	3559.9†	3505.2†	3499.1†	3474.7†	3427.0†
3338.9†	3305.4†	3267.60	3232.61	3029.91	2980.2†	2965.6†
2913.1†	2890.7†	2878.01	2790.0†	2770.04	2719.00	2682.86
2670.73	2652.70	2631.6†	2616.7†	2612.40	2598.16	2528.60
2506.9†	2445.59	2383.71	2373.78	2360.60	2311.60	2306.56
2262.55	2179.33	2175.99	2098.47	2068.54		

ARGON.

Argon was isolated from the atmosphere in 1894 by Rayleigh and Ramsay.² The pure gas, in a Geissler tube, exhibits several lineal spectra depending on the pressure in the tube and on the nature of the electric discharge. Crookes³ discovered two of these, and from the predominant color of their light termed them the red and the blue spectrum respectively. Eder and Valenta⁴ have observed a third spectrum, which they term the white. It is produced by the use of very large condensers in conjunction with a powerful induction-coil and a strong current. In these circumstances, under a pressure of 15–20 mm., white light is emitted from the capillary. Spectroscopically the light is peculiar; the majority of the lines become widened, and few remain sharp, many coincide with lines in the blue and red spectra, but

¹ P. R. S. (1875) **23**, 344.

² P. T. (1895) **186**, 221.

³ C. N. (1895) **72**, 66, 99.

⁴ Sitzungsbericht d. Wiener Akad. Mathem.-Naturw. (1895) **404**. Denkschr. d. Wiener Akad. (1896) **64**.

* Visible only in the spark-spectrum. (Thalén.)

† Visible only in the spark-spectrum. (Hartley and Adeney.)

certain groups are displaced from 0.5–1 Ångström towards the red. At present Eder and Valenta are unable to suggest the cause of this partial displacement, but it appears to be connected with the pressure and temperature of the gas, and with the nature of the electric discharge. There is still some doubt as to whether argon is an element or a mixture of two. Dewar, and subsequently Berthelot have suggested that it is an allotropic modification of nitrogen, but later work does not lend confirmation to this view. The gas obtained from clèveite, which was formerly supposed to be nitrogen, has been shown by Ramsay to exhibit all the lines of atmospheric argon together with several others including the D_3 -line of helium; but atmospheric argon contains at least three bright lines in the violet which are not shown by the gas from clèveite; hence Ramsay concludes that atmospheric argon is probably a mixture. Berthelot¹ obtained a fluorescent spectrum by the action of a moderately strong induction-current on a mixture of argon, benzene vapor, and mercury in a Geissler tube; the spectrum differs from that given by any other gas, and the yellow and green rays were perfectly visible in the spectroscope in full daylight. He considers that the spectrum is that of a compound of argon and mercury with the constituents of benzene, but Dorn and Erdmann² found that some of the lines were those of mercury and nitrogen. Eder and Valenta³ have photographed the argon spectrum between $\lambda = 5060$ and $3320\mu\mu$, using a powerful concave grating, and Kayser⁴ has published a preliminary list of the lines in the blue spectrum, the gas being obtained from the atmosphere; the lines observed are not given in Rowland's Atlas and reproductions of the Fraunhofer lines.

¹ C. r. (1895) **120**, 662, 797, 1049, 1386; (1897) **124**, 113.

² Lieb. Ann. (1895) **287**, 230.

³ Wiener Akadem. Anzeiger (1895), No. 21.

⁴ C. N. (1895) **72**, 99. Sitzungsber. d. Berl. Akad. (1896) **24**. See also Newall, C. N. **71**, 115.

Trowbridge and Richards¹ find that the oscillatory discharge of the condenser is an important factor in producing the blue spectrum of argon. The pure red spectrum is obtained if the tube is connected with the terminals of an electric machine; but if the spark-gap is interposed, the spectrum changes at once to blue.

Red spectrum:

7723.4	7635.6	7515.4	7383.9	7066.6	6964.8	6415.2
6031.5	5739.87	5651.03	5607.44	5597.89	5572.87	5559.02
5506.42	5496.16	5451.95	5421.68	5221.65	5187.47	5162.59
4888.21	4702.40	4628.60	4596.30	4522.49	4510.90	4345.27
4335.42	4333.65	4300.18	4272.29	4266.44	4259.50	4251.27
4200.75	4198.40	(4191.02)	4190.85)	4182.03	4164.36	4158.65
4152.97	4054.65	4046.04	4044.52	3949.08	3947.75	3894.78
3834.83	3781.07	3680.30	3678.43	3649.99	3634.64	3632.82
3606.69	3588.64	3567.88	3564.54	3563.50	3554.48	3461.23
3394.03	3034.7	3021.9	2967.3	2614.6	2516.3	2478.65

Blue spectrum:

6644.2	6059.5	6043.0	6031.5	5651.03	5607.44	5559.02
5496.16	5287.24	5166.03	5145.57	5142.20	5062.35	5017.46
5009.63	4965.38	4933.49	4880.14	4866.14	4847.94	4806.17
4765.04	4736.03	4658.04	4637.35	4609.73	4590.05	4579.53
4545.26	4503.15	4481.99	4426.16	4401.19	4400.25	4379.79
4371.46	4370.92	4352.40	4348.11	4331.31	4283.03	4277.65
4266.44	4237.34	4228.27	4222.76	4182.97*	4179.45	4178.58
4175.25*	4174.20*	4172.95*	4172.05*	4156.30	4131.95	4113.04
4104.10	4082.59	4079.80	4076.85	4072.58	4072.18	4053.12
4043.04	4038.99	4035.58	4033.99	4013.97	3992.17	3979.57
3974.70	3946.20	3944.50	3932.71	3931.32	3928.78	3925.93
3914.93	3911.69	3907.80	3892.15	3891.53	3880.46	3875.40
3872.26	3868.68	3850.70	3845.51	3841.63	3830.58	3826.92
3809.58	3808.72	3803.38	3799.65	3795.56*	3786.60	3781.07
3766.30	3765.48	3763.76	3753.60	3738.04	3734.70	3729.52
3720.61	3718.39	3717.36	3660.70	3656.26	3655.52	3651.04
3640.00	3637.25	3622.31	3588.64	3582.54	3581.82	3576.80
3565.20	3561.20	3559.69	3548.69	3546.03	3545.78	3535.53
3522.14	3521.46	3520.15	3514.53	3509.93	3491.71	3480.69
3478.42	3476.96	3464.33	3454.30	3421.80	3391.86*	3388.65

¹ Amer. Jour. Sci. 1897 [4] 3, 15. P. M. 43, 77. See also Friedländer, Zeit. f. phys. Chem. (1896) 19, 662.

* Visible only by the use of powerful condensers, otherwise absent from the normal blue spectrum.

3376.61	3351.10	3307.37	3301.97	3293.82	3285.91	3281.83
3263.71	3204.49	3181.26	3169.88	3161.64	3139.26	3093.57
3029.10	2979.35	2955.67	2943.17	2924.92	2896.97	2891.87
2866.0	2806.3	2769.7	2753.9	2744.88	2732.67	2708.40
2647.6	2562.3	2544.8	2534.8	2516.8	2515.6	2500.4
2491.0	2480.9	2479.2	2454.5	2438.8	2415.7	2395.7
2364.2	2350.6	2344.4	2337.8	2331.7	2316.5	2314.0
2309.4	2282.6	2252.4	2243.7	2234.7	2219.9	2175.6
2171.5	2165.8	2130.6	2050.5			

White spectrum:

5306.04	5287.24	5166.03	5145.57	5142.20	5062.35	5017.46
5009.63	4972.40	4965.38	4933.49	4888.88	4880.14	4867.72
4847.94	4806.17	4765.04	4736.03	4727.00	4658.04	4609.75
4590.04	4579.53	4545.26	4481.99	4430.35	4426.16	4401.19
4400.25	4379.79	4371.46	4370.92	4352.40	4348.11	4332.20
4331.31	4278.02	4266.44	4228.27	4104.93	4072.3	4013.97
3933.40	3928.78	3892.15	3869.50	3850.70	3827.67	3781.58
3766.21	3729.52	3589.11	3582.79	3577.27	3561.50	3560.15
3546.58	3514.98	3510.26	3491.71	3477.38	3388.94	3377.38
3351.80	3294.58					

ARSENIC.

The spark-spectrum of arsenic is obtained by the use of the vapor of the element, or of the chloride contained in a Geissler tube. The arc-spectrum differs from that of the spark, and exhibits no lines in the visible field; the portion from $600\mu\mu$ onwards has been photographed by Kayser and Runge;¹ between $300\mu\mu$ and $200\mu\mu$ the lines are numerous though not very strong, but they are often observed, showing the wide distribution of arsenic, and its frequent occurrence as an impurity; indeed the lines $\lambda = 2349$ and 2288 , which are the strongest, are rarely absent from any spectrum of a carbon arc. Lockyer² and Ciamician³ have described a channelled absorption-spectrum.

¹ A. B. A. 1893.

² C. r. (1874) **78**, 1790.

³ Wien. Ber. **76**, 499; **78**, 867; **82**, 425. See also Thalén, N. A. S. U. (1868) [3] **6**. Hartley and Adeney, P. T. (1884) **175**, 124. Kirchhoff, A. B. A. 1861. Huggins, P. T. (1864) **154**, 139. Plücker and Hittorf, P. T. **155**, 1. Ditte, C. r. (1871) **73**, 738. Huntingdon, Sillim. Jour. (1881) **22**, 214.

Arc and spark spectra:

6170.7*	6111.2*	5652.1*	5559.2*	5499.1*	5332.1*	4494.7†
4467.0†	4459.4†	4431.7†	4036.7†	3949.2†	3931.4†	3922.3†
3825.1†	3785.0†	3119.69	3075.44	3057.7†	3053.0†	3032.96
2991.11	2898.83	2860.54	2830.2†	2780.30	2745.09	2601.2†
2528.3†	2526.4†	2492.98	2456.61	2437.30	2381.28	2370.85
2369.75	2349.92	2288.19	2271.46	2228.77	2165.64	2157.1†
2148.2†	2144.2†	2133.92	2113.14	2067.26	2009.31	

BARIUM.

The spark-spectrum of barium has been investigated by Kirchhoff,¹ Huggins,² Thalén,³ and Lecoq de Boisbaudran;⁴ the arc-spectrum by Lockyer,⁵ Liveing and Dewar,⁶ and, most accurately, by Kayser and Runge,⁷ who employed the chloride and carbonate, and measured 162 lines. Barium compounds are gradually dissociated in a hot Bunsen flame, and all exhibit the band-spectrum of the oxide, together with line $\lambda = 5535.69$ of the metal. Immediately on their introduction the haloïd derivatives produce their own peculiar fugitive spectra; these can always be obtained with certainty if a wire holding ammonium chloride is placed in the flame below the specimen of barium salt under examination. For prolonged experiments hydrogen chloride, hydrogen bromide, or iodine vapor must be introduced into the flame. The flame-spectra of these compounds have been studied by Mitscherlich⁸ and Lecoq de Boisbaudran.

¹ A. B. A. 1861.

² P. T. (1864) **154**, 139.

³ N. A. S. U. (1868) [3] **6**.

⁴ Spectres lumineux (Paris, 1874).

⁵ P. T. **163**, 369; **164**, 806.

⁶ *Ibid.* (1883) **174**, 216.

⁷ A. B. A. 1891.

⁸ P. A. (1862) **116**, 419; (1863) **121**, 459. For the flame-spectrum see also Bunsen and Kirchhoff, P. A. **110**, 161. Bunsen, P. A. (1875) **155**, 366.

* Only visible in the spark-spectrum. (Thalén.)

† Only visible in the spark-spectrum. (Hartley and Adeney.)

Arc and spark spectra:

6497.07	6141.93	6111.01	6063.33	6019.69	5971.94	5907.88
5853.91	5826.50	5805.86	5800.48	5777.84	5680.34	5535.69
5519.37	5424.82	5267.20	4934.24	4903.11	4900.13	4726.63
4700.64	4691.74	4673.69	4579.84	4574.08	4554.21	4525.19
4523.48	4506.11	4432.13	4402.75	4350.49	4283.27	4130.88
3995.92	3993.60	3938.09	3935.87	3910.04	3891.97	3611.17
3599.60	3544.94	3525.23	3501.29	3357.00	3071.71	2785.22
2771.51	2634.91	2347.67	2335.33	2304.32		

Flame-spectra:

Barium bromide....	5411	5359	(5305	5250)	5207	5150
Barium chloride	5314	5243	(5206	5172)	5137	
Barium iodide.....	5608	5377				
Barium oxide	6450	6298	(6240	6179	6109	6032)
	(5939	5868)	5825	(5769	5720	5648)
	5535.69*	5493	5347	5216	5090	4874

BERYLLIUM.

The whole of the spectrum of this element has not hitherto been thoroughly investigated; some of the visible lines in the spark-spectrum have been measured by Thalén¹ and Kirchhoff,² and Hartley³ has observed others in the ultra-violet. Cornu⁴ mentions two lines in the arc-spectrum, and Crookes⁵ states that, when caused to fluoresce in a vacuum, a continuous blue spectrum is produced. Rowland and Tatnall⁶ have recently examined the arc-spectrum between $\lambda = 2100-4600$; the lines are comparatively feeble.

Arc and spark spectra:

4572.869†	4489.4†	3905.2†	3322.3†	(3321.486	3321.218)†
(3131.200	3130.556)	(2651.042	2650.414)	2649.8†	(2494.960
2494.532)	2493.6†	2478.1†	2348.698		

¹ N. A. S. U. (1868) [3] 6.² A. B. A. 1861.³ J. Chem. Soc. 43, 316.⁴ Spectre normal du soleil (Paris, 1881).⁵ A. c. p. [5] 23, 555. See also Lockyer, P. R. S. 27, 280. Ciamician, Wien. Ber. [2] 82, 425.⁶ Astrophys. Jour. (1895) 1, 16; 2, 185.

* Due to the metal itself.

† Spark spectrum.

BISMUTH.

The spark spectrum is obtained by the use of bismuth electrodes, and has been measured by Huggins,¹ Thalén,² and Hartley and Adeney;³ the arc-spectrum by Liveing and Dewar,⁴ and recently, commencing at $618\mu\mu$, by Kayser and Runge.⁵ The spark-spectrum exhibits many lines that are absent from that of the arc. Bismuth salts, moistened with hydrochloric acid, produce in the Bunsen flame a fugitive band-spectrum of the oxide. The spectra of the compounds themselves are obtained by volatilizing them in a hydrogen flame. They have been drawn by Mitscherlich.⁶

Arc and spark spectra:

6493.8*	6130.2*	6057.7*	5862.6*	5817.1*	5717.6*	5552.44	5451.0*
5271.1*	5209.0*	5144.0*	5124.5*	4993.9*	4722.72	4560.9*	4302.6*
4260.1*	(4122.01	4121.69)	4079.7†	3864.4†	3793.3†	3757.6†	3695.7†
3654.7†	3614.6†	3596.26	3115.2†	3067.81	3024.75	2993.46	2989.15
2938.41	2898.08	2809.74	2784.4†	2780.57	2766.7†	2730.61	2696.84
2627.99	2524.58	2515.72	2489.5	2400.98	2276.64	2230.70	2228.31
2203.2	2189.70	2187.4†	2176.70	2157.03	2152.98	2134.38	2133.72
2110.35	2061.77						

BISMUTH OXIDE.

Flame-spectrum. The bands are measured from the red.

6383	6195	6040	5874	5718	5583	5445	5329	5221
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BORON.

According to Kayser and Runge⁷ the arc-spectrum of this element consists of only two lines, which, together with a

¹ P. T. (1864) p. 139.

² N. A. S. U. (1868) [3] 6.

³ P. T. (1884) **175**, 130.

⁴ *Ibid.* (1883) **174**, 222. P. R. S. **29**, 398.

⁵ A. B. A. 1893.

⁶ P. A. (1863) **121**, 459. See also Ångström, *Ibid.* (1855) **94**, 141. Mascart, Ann. de l'École normale (1866), **4**, 7. E. Becquerel, C. r. **96**, 1218; **97**, 72.

⁷ A. B. A. 1892.

* Visible only in the spark-spectrum. (Thalén.)

† Visible only in the spark-spectrum. (Hartley and Adeney.)

third, have also been observed by Hartley¹ in the spark-spectrum; Eder and Valenta² found, however, fourteen additional lines, the majority of which are double, and confirmed the presence of four that had been detected by Ciamician.³ Rowland and Tatnall⁴ have recently photographed the arc-spectrum between $\lambda = 2100-4400$. Only the double line could be detected; the numerous bands are probably due to some compound, such as boric anhydride. Boric acid and its salts produce a characteristic band spectrum in the Bunsen flame.

Arc and spark spectra:

3450.8* (2497.821 2496.867) 2267.0† 2266.4†

BORIC ACID.⁵

The wave-length is measured at the middle of the bands.

Flame-spectrum:

6398	6211	6032	5808	5481	5440
5193	4912	4722	4530		

BROMINE.

Bromine vapor gives a line-spectrum with the electric spark,⁶ but the measurements of it are only approximate. Its absorption-spectrum at the ordinary temperature has been accurately investigated by Hasselberg;⁷ when a high disper-

¹ P. R. S. 35, 301.

² Denkschr. d. Wien. Akad. (1893) 60, 307.

³ Sitzber. d. Akad. d. Wiss. zu Wien. [2] 82, 425. See also Troost and Hautefeuille, C. r. (1871) 73, 620. Salet, A. c. p. (1873) [4] 28, 59.

⁴ Astrophys. Jour. (1895) 1, 16.

⁵ Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Thalén, Upsal. Universit. Arsskrift. 1866. Also Salet and Eder, and Valenta, as above.

⁶ Salet, Spectroscopie (Paris, 1888). A. c. p. [4] 28, 26. Plücker, P. A. 105, 527; 107, 87. Plücker and Hittorf. P. T. 155, 1. Ciamician, Wien. Ber. 76 [2], 499; 77 [2], 839; 78 [2], 867.

⁷ K. Svensk. Akad. Handlingar. (1891) 24, No. 3. Mém. de l'acad. de St. Petersb. (1878) 26, No. 4. See also Daniell and Miller, P. A. 28, 386. Roscoe and Thorpe, P. T. 167, 209. Moser, P. A. 160, 188.

* Visible only in the spark-spectrum. (Hartley.)

† Visible only in the spark-spectrum. (Eder and Valenta.)

sion is employed it is seen to consist of a large number of fine lines grouped into bands.

The spectrum obtained with a continuous discharge differs from that produced when a condenser is included in the circuit.¹

Spark-spectrum of bromine vapor:

7000*	6780*	6630*	6583	6559	6546	6353
6148	5876	5830	5723	5590	(5509)	5497
5491)	(5450	5423)	(5327	5305	5240	5184
5166)	5060	4930	(4816	4788)	4705	4677
4618	4366	3980				

Absorption-spectrum:

Group 6162—6142:	6158.09	6155.45	6154.19	6150.57	6148.15
Group 6142—6122:	6125.12	6124.01			
Group 6122—6103:	6117.61	b (6116.47	6115.67)	6108.49	
Group 6103—6079:	6083.20	6082.50	6080.36	6079.78	
Group 6079—6066:	6077.85	6069.61			
Group 6066—6042:	6064.50	6055.95	6055.76	6055.22	6054.78
	6054.25				
Group 6042—6003:	6021.02	6020.15	6018.40	6017.73	b (6017.18
	6016.56)	6013.46	(6011.28	6011.02)	6008.26
	6008.03				
Group 6003—5977:	5982.65	5982.34	5981.55	5981.30	5980.25
Group 5977—5949:	5966.29	5964.97	5964.35	5961.44	5961.06
	5960.54	5960.16	5959.22	5958.32	
Group 5949—5935:	5942.73				
Group 5935—5896:	5929.33	5924.62	5924.23	5924.00	5906.13
	5904.36	5903.69	5898.45		
Group 5896—5862:	5869.91				
Group 5862—5832:	5854.95	5846.34	5844.78	5843.44	5838.81
	5838.16	5837.59	5836.95	5836.41	5832.43
Group 5832—5807:	5828.60	5812.41	5812.18	5809.57	5808.87
	5808.15	5807.95			
Group 5807—5791:	5802.82	5802.26	5800.93	5798.15	5796.81
	5795.64	5795.44			
Group 5791—5763:	5782.46	5782.01	5777.39	5774.75	5773.90
	5773.02	5771.29	5765.71	5765.03	5764.42
Group 5763—5742:	5760.33	5748.57	5747.55	5744.46	5742.54

¹ Trowbridge and Richards, Amer. Jour. Sci. (1897) [4] 3, 117. P. M. 43, 135.

* Inaccurate.

Group 5742—5712:	5739.81	5738.91	5738.11	5737.25	5736.49
	5730.97	5729.69	b (5727.63)	5726.98	5726.14
	5725.79	5725.54	5715.38	5712.44	5712.18
Group 5712—5688:	5711.38	5702.53	5701.83	5698.62	5697.29
	5693.89				
Group 5688—5659:	5678.02	5676.93	5667.97	5667.20	5666.46
	(5664.31)	5664.06)	5663.52	5659.37	
Group 5659—5616:	5657.45	5656.93	5647.46	5646.42	5634.43
	5617.61				
Group 5616—5587:	5603.27	5602.44	5598.70	5596.17	5595.69
	5595.17	5592.68			
Group 5587—5555:	5573.63	5572.93	5572.73	b (5570.47)	5569.90
	5569.56)	(5566.75	5566.33)	5565.97	5563.90
	5563.00	5561.35	5550.44	5560.16	5559.86
	5557.42	5556.93	5556.39	5556.03	5555.86
Group 5555—5528:	5542.08	5530.65			
Group 5528—5502:	(5506.88	5506.36)	5504.72	5503.62	
Group 5502—5477:	5500.58	5498.60	5496.41	(5491.98	5491.36)
	(5485.19	5484.93)	(5482.70	5482.53)	5482.17
	5479.32	5478.96			
Group 5477—5456:	5468.94	5467.24	(5466.84	5466.71)	5464.96
	5461.81	5460.74	5460.19	5457.15	5456.89
Group 5456—5430:	5455.62	5442.86	5439.75	(5436.98	5436.74)
	5432.25				
Group 5430—5406:	5420.61	5418.23	5417.50	5417.03	5415.96
	5414.76	5413.91	5410.93	5408.91	
Group 5406—5372:	5390.90	5389.92	5377.93	5375.92	5372.30
	5372.11				
Group 5372—5354:	5356.49	5353.80			
Group 5354—5333:	(5348.06	5347.87)	5342.38	5341.82	5340.92
	(5338.31	5338.07)	5333.11		
Group 5333—5317:	(5329.60	5329.30)	(5319.77	5319.56)	
Group 5317—5289:	(5290.47	5290.21)			
Group 5262—5243:	5256.32	5255.79	5251.87	5249.73	5248.80
	5247.61	5245.33			
Group 5243—5215:	5241.88	5241.72	5234.00	5215.92	
Group 5184—5159:	5184.57	5184.29	5183.60	5178.56	5174.91
	5168.26	5167.41	5163.35	5160.54	

CADMIUM.

The references given below show how numerous have been the investigations of the cadmium-spectrum; the latest are those of Kayser and Runge,¹ who occasionally employed the

¹ A. B. A. 1891.

chloride, but usually the metal. The arc-spectrum differs considerably from that of the spark; the latter exhibits a pair of lines of the highest intensity of $\lambda = 5378.8$ and 5338.3 , which are absent from the former, and the same applies to 90 lines of inferior brightness between $\lambda = 4215$ and 2111 which have been measured by Hartley and Adeney.¹ Cadmium chloride and bromide are dissociated in the Bunsen flame, and exhibit the lines $\lambda = 5086$, 4800 , and 4678 .

Arc and spark spectra:

6467.3*	6438.8*	5378.8*	5338.3*	5154.85	5086.06†	4800.09†
4678.37†	4662.69	4413.23	3613.04	3610.66	3467.76	3466.33
3403.74	3261.17	(3252.63)	3133.29	3081.03)	2980.75	2880.88
2763.99	2639.63	2601.99	2573.12	2329.35	2312.95	2288.10
2267.53	2239.93	2194.67	2144.45			

CÆSIUM.²

Bunsen and Kirchhoff discovered cæsium in 1861 by means of spectrum analysis. Its salts are all dissociated in the Bunsen flame, and exhibit the lines of the metal; the more prominent ones are $\lambda = 4555$ and 4593 in the blue, and $\lambda = 6010$ in the orange.

Arc, spark, and flame spectra:

6973.9	6723.6	6213.4	6010.6	5845.1	5664.0	5635.1
4593.34	4555.44	3888.83	3876.73	3617.08	3611.84	

¹ P. T. (1883) **175**, 98. See also Thalén, N. A. S. U. (1868) [3] **6**. Kirchhoff, A. B. A. 1861. Mascart, Annales de l'Ecole normale (1866), **15**. Lockyer, P. T. (1873) **163**, 369. Cornu. Journ. de Phys. (1881) **10**, 425. Liveing and Dewar, P. R. S. (1879) **29**, 482. P. T. (1888) **179**, 231. Ames, P. M. (1890) [5] **30**, 33. Bell, Am. Journal of Sciences, June, 1886.

² Kayser and Runge, A. B. A. 1890. Bunsen, P. A. **119**, 1; **155**, 366. Johnson and Allen, P. M. [4] **25**, 199. Thalén, N. A. S. U. (1868) [3] **6**. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Lockyer, P. R. S. (1878) **27**, 280. Liveing and Dewar, *Ibid.* (1879) **28**, 352.

* Only visible in the spark spectrum. (Thalén.)

† Visible also in the flame spectrum of the chloride and bromide. (Lecoq de Boisbaudran.)

CALCIUM.

The line-spectrum of calcium has been measured by Kirchhoff,¹ Huggins,² Thalén,³ Lecoq de Boisbaudran,⁴ Lockyer,⁵ Cornu,⁶ Liveing and Dewar,⁷ and more recently by Kayser and Runge,⁸ who employed the electric arc and calcium chloride. The faint bands which occasionally appear in the yellow and red when the arc is used are considered by Lecoq de Boisbaudran to be due to oxide. Many of the calcium lines are readily produced, and are therefore always visible when carbon electrodes are employed. H. Becquerel⁹ observed bands from $\lambda = 8880$ – 8830 and from $\lambda = 8760$ – 8580 in the infra-red. The haloïd compounds have been investigated by Bunsen, Mitscherlich,¹⁰ and Lecoq de Boisbaudran;¹¹ in the Bunsen flame some bands peculiar to each compound are visible, together with those of the oxide and the blue line, $\lambda = 4226.91$, of the metal. The oxide bands are also produced if the flame is charged with hydrogen chloride, hydrogen bromide, hydrogen iodide, or hydrogen fluoride.

Arc and spark spectra:

6499.85	6462.75	6439.36	6169.87	6162.46	6122.46	6102.99
5867.94	5857.77	5603.06	5601.51	5598.68	5594.64	5590.30
5588.96	5582.16	5513.07	5349.66	5270.45	5265.79	5264.46
5262.48	5261.93	5189.05	5041.93	4878.34	4586.12	4581.66
4578.82	4527.17	4456.08	4454.97	4435.86	4435.13	4425.61

¹ A. B. A. 1861.

² P. T. (1864) **154**, 139.

³ N. A. S. U. (1868) [3] **6**. Spectre du fer (Upsala, 1884).

⁴ Spectres lumineux (Paris, 1874).

⁵ P. T. (1874) **164**, 809. C. r. **82**, 660.

⁶ Spectre norm. du soleil (Paris, 1881).

⁷ P. T. (1882) **174**, 187. P. R. S. **28**, 367, 475; **29**, 398.

⁸ A. B. A. 1891. See also Mascart, Ann. de l'école normale (1866), **15**. Ångström, Recherches sur le spectre solaire (Upsal, 1868). Eder and Valenta, Phot. Corresp. 1893, p. 59. Rydberg, W. A. (1894) **52**, 119.

⁹ C. r. **94**, 1218; **97**, 72.

¹⁰ P. A. **121**, 459

¹¹ Spectres lumineux (Paris, 1874).

4355.41	4318.80	4307.91	4302.68	4299.14	4289.51	4283.16
4226 91*	3973.89	3968.63	3957.23	3933.83	3644.45	3630.82
3624.15	3487.76	3361.92	3350.22	3344.49	3179.45	3158.98
2398.66	2275.60					

CALCIUM BROMIDE.

Flame-spectrum:

6267 6243 6103

CALCIUM CHLORIDE.

Flame-spectrum:

6266	(6203	6182)	(6069	6045)	5934
5817	(5544	5518)†			

CALCIUM FLUORIDE.

Flame-spectrum:

6061 6027 5329 5302

CALCIUM OXIDE.

Flame-spectrum:

6221 5996 (5544 5518)

CARBON.

This element has been more frequently investigated than any other; its spectra are extremely complex, but it is now generally acknowledged to exhibit two, a line and a band spectrum. The former is produced by the passage of sparks from a Leyden jar through carbon dioxide or carbon monoxide; its visible portion, between wave-length 3920–2266.5, has been measured by Ångström and Thalén,¹ and the ultra-violet part by Liveing and Dewar.² The band-spectrum has also been termed the “flame-spectrum,” or “Swan’s spectrum”; it was first observed by Wollaston³ in 1802, and then

¹ N. A. S. U. (1875) [3] 9.

² P. R. S. (1880) 30, 152, 494; (1882) 33, 403; (1883) 34, 123. P. T. (1882) 174, 187. Also Eder and Valenta, Denkschr. Wiener Akad. (1893) 60.

³ P. T. 1802.

* Also visible in the Bunsen flame. † Probably due to the oxide.

investigated by Swan¹ from 1850 onwards. In common with Ångström, Thalén,² and Liveing and Dewar,³ he ascribed it to hydrocarbons, but the last workers, together with Attfield,⁴ Morren,⁵ and Dibbits,⁶ subsequently recognized that it was due to carbon, since it is produced by the combustion of pure cyanogen in dry oxygen. This band-spectrum consists of five complex bands, with the following wave-lengths according to Ångström and Thalén, and Watts:⁷

1 or orange band.	2 or greenish-yellow band.	3 or green band.	4 or blue band.	5 or indigo band
6187-5954	5633-5425	5164-5082	4736-4677	4381-4232

The three medial bands have been recently measured by Fiévez,⁸ and the green one by Kayser and Runge;⁹ for the others there are only the old observations of Watts, Ångström and Thalén, and Piazz-Smyth¹⁰ available. In addition to the above bands others are sometimes observed in the arc; they occur in the blue, violet, and ultra-violet, and have the following wave-lengths:

I Band.	II Band.	III Band.	IV Band.	V Band.
4600-4500	4290-4150	3884-3850	3590-3550	3370-3350

Their existence in the arc is doubted by Kayser and Runge; Liveing and Dewar have ascribed them to cyanogen, whilst Lockyer,¹¹ H. W. Vogel, and others regard them as a

¹ P. T. E. (1857) **21**, 411.

² N. A. S. U. (1875) **9**.

³ P. R. S. (1880) **30**, 152, 494; (1882) **33**, 403; (1883) **34**, 123. P. T. (1882) **174**, 187.

⁴ *Ibid.* (1862) **152**, 221. P. M. (1875) **49**, 106.

⁵ A. c. p. (1865) [4] **4**, 305.

⁶ P. A. (1864) **122**, 497.

⁷ P. M. (1869) [4] **38**, 249; **45**, 12; (1874) **48**, 369, 456; (1875) **49**, 104.

⁸ Mém. de l'Acad. roy. de Belgique (1885), **47**.

⁹ A. B. A. 1889.

¹⁰ Astr. Obs. Edinb. (1871) **13**, 58. P. M. (1875) [4] **49**, 24; (1879) [5] **8**, 107. P. T. E. **30**, 93.

¹¹ P. R. S. (1878) **28**, 308; (1880) **30**, 335. See also Plücker, P. A. (1858) **105**, 77; (1859) **107**, 533, and with Hittorf, P. T. **155**, 1. Jahresber. (1864) p. 110. Van der Willigen, P. A. (1859) **107**, 473. Huggins, P. T. (1868)

second band-spectrum of carbon produced only at high temperatures. Kayser at first shared this view, but experiments made in conjunction with Runge led to a different conclusion. A strong current of carbon dioxide was directed on to the arc, whereupon the cyanogen bands became fainter and disappeared. In order to prove that this was not due to a lowering of the temperature a still stronger current of air was substituted for the carbon dioxide: the bands immediately increased in brightness in consequence of the additional supply of nitrogen. The view that the cyanogen bands are essentially due to carbon is supported by their occurrence in comets, and in the solar spectrum; this last fact was long doubted, but was established by Rowland. That the spectrum of a compound which is dissociated at 1000° should be visible in the solar spectrum appears somewhat paradoxical, but Kayser and Runge have pointed out that the carbon molecule, as is shown by its varying specific heat, is not a constant quantity, and the "cyanogen bands" may be the spectrum of an unknown compound of carbon and nitrogen which is capable of existence at very high temperatures. The cyanogen bands have been measured by Liveing and Dewar, and the third, fourth, and fifth ones also by Kayser and Runge.

The carbon bands all have their brighter edges directed towards the red end of the spectrum; each possesses a number of edges, varying from three to seven, which become weaker towards the violet. The lines extend from the first edge of one band to the beginning of the next, so that no portion of the spectrum from $620\mu\mu$ to $340\mu\mu$ is free from carbon lines, the total number of which is at least 10,000. Metallic spectra obtained by means of the arc and carbon poles always exhibit

158, 558. Lielegg, *Wien. Ber.* (1868) **52**, 593. Troost and Hautefeuille, *C. r.* (1871) **73**, 620. Wüllner, *P. A.* (1872) **144**, 481. Salet, *A. c. p.* (1873) [4] **28**, 60. Lecoq de Boisbaudran, *Spectres lumineux* (Paris, 1874). Wesendonck, *Inaug.-Diss.* (Berlin, 1881). Hartley, *B. A. R.* 1883. Eder, *Denkschr. Wiener Akad.* (1890) **57**.

the metallic lines superposed by the carbon bands, hence a good knowledge of the latter is very desirable.

Line-spectrum:

6584.0	6578.5	5695.1	5661.9	5647.5	5145.0
4266.6	3920.0	2837.2	2836.3	2746.5	2511.9
2509.0	2478.3	2296.5			

Band-spectrum:

I. Orange Band 6187—5954:	6188.2	6119.9	6057.3	6001.8	5954.5		
II. Green-yellow Band:							
1. Edge:	5635.3	5634.3	5633.9	5633.4	5632.9	5632.2	5631.6
	5630.9	5630.1	5629.3	5628.5	5627.6	5626.7	5625.8
	5624.4	5623.1	5620.4	5619.6	5618.8	5617.8	5615.6
	5613.8	5611.8	5610.1	5608.5	5606.1	5603.5	5600.8
	5598.0	5595.3	5592.5	5589.7	5588.1	5587.4	5585.5
2. Edge:	5584.4	5582.1	5578.8	5578.5	5578.2	5577.1	5575.5
	5573.2	5572.8	5572.4	5571.1	5570.1	5569.5	5568.3
	5567.2	5566.7	5565.0	5564.3	5563.9	5563.5	5561.4
	5560.5	5560.0	5558.1	5556.3	5556.0	5555.7	5554.1
	5552.9	5552.6	5540.9	(3. Edge).			
III. Green Band:							
1. Edge:	5165.4	5165.2	5164.9	5164.6	5164.5	5163.7	5163.2
	5162.7	5162.5	5162.0	5161.3	5160.5	5160.0	5158.7
	5157.8	5157.3	5156.2	5155.3	5154.5	5154.4	5153.4
	5153.0	5152.6	5152.0	5150.8	5149.2	5147.8	5146.2
	5144.7	5143.0	5141.3	5139.4	5137.7	5135.7	5133.8
	5131.7	5129.7	5129.4				
2. Edge:	5129.4	5129.3	5129.0	5128.8	5127.8	5127.4	5126.2
	5125.4	5124.9	5123.9	5122.9	5121.8	5121.6	5119.3
	5118.2	5116.8	5115.9	5114.4	5113.2	5111.8	5110.8
	5110.2	5109.2	5108.0	5106.5	5105.5	5103.9	5103.5
	5102.6	5101.0	5099.9	5098.2	5096.9	5095.3	5094.2
	5092.4	5091.6	5091.0	5089.3	5087.6	5087.1	5086.4
	5084.9	5083.1	5081.9	5080.1	5078.5	5076.8	5071.9
	5070.1	5068.8	5066.9	5066.1	5065.1	5063.7	5058.1
	5056.3	5054.8	5052.8	5049.7	5045.4	5041.5	5039.9
	5037.9	(5033.9	5033.7)	5032.2	5030.1	5026.0	5024.1
	5022.1	5017.9	5013.9	5009.6	5005.6	5001.1	4997.0
	4992.5	4988.3	4983.7	4979.4	4974.6	4970.3	4965.4
	4961.0	4956.1	4951.6	4946.5	4886.2	4854.2	4849.0
	4838.0	4809.7	4804.4	4798.4			
IV. Blue Band:							
1. Edge:	4737.2	4736.4	4735.9	4735.5	4735.1	4734.6	4734.1
	4733.6	4733.0	4732.4	4732.0	4731.0	4730.0	4729.4

	4728.4	4727.1	4726.2	4725.1	4724.0	4723.6	4722.3
	4721.2	4719.9	4718.8	4717.4	4716.8	4715.4	
2. Edge:	4715.2	4714.1	4713.3	4711.7	4710.5	4708.6	4707.2
	4706.9	4705.9	4704.0	4702.6	4702.1	4699.9	4699.4
	4698.4	4697.6					
3. Edge:	4697.2	4695.6	4695.3	4694.2	4693.9	4692.8	4691.2
	4690.7	4689.5	4688.3	4687.4	4686.2	4685.0	
4. Edge:	4684.7	4683.2	4682.5	4682.0	4681.0	4679.8	4679.5
	4677.6	4675.8	4675.0	4674.1	4673.8	4673.1	4672.8
	4671.8	4671.4	4671.0	4670.4	4669.8	4669.2	4668.6
	4667.7	4666.9	4666.5	4665.6	4664.4	4664.1	4663.0
	4661.3	4659.9	4658.9	4657.9	4657.1	4656.8	4654.6
	4653.7	4652.3	4652.0				

V. Band: 1. Edge 4382.0 2. Edge 4371.4 3. Edge 4365.1

CARBON MONOXIDE.¹

6079	5609	5198 b ^r	5187.5	5184.5	5182.5	5179.5	
5176.0	5173.5	5170	5167.2	4834.5 b ^r	4823.5 b	4821.3 b	
4819.1 b	4817.0 b	(4789.8 b	4786.5 b)	4509.8 b ^r	4394.7 b ^r	(A. and Th.)	
3493.3 b ^r	3307.5 b ^r	3134.6 b ^r	2976.3 b^r	3832.0 b^r	2792.7 b^r	2665.1 b ^r	
2599.0 b ^v	2510.8 b ^v	2435.0 b ^v	2425.0 b ^v	2404.7 b ^v	2394.0 b ^v	2381.5 b ^v	
2364.8 b ^v	2337.7 b ^v	2311.4 b ^v	2286.2 b ^v	2220 b ^v	2215.3 b^v	2188.1 b ^v	
2172.3 b ^v	2161.6 b ^v	2149.9 b ^v	2127.8 b ^v	2112.7 b ^v	2089.3 b ^r	2066.8 b ^v	

(Deslandres).

The bands marked b^r are sharply defined towards the red and shade off towards the violet; those marked b^v are sharply defined towards the violet and shade off towards the red.

CYANOGEN.²

I. Band:

4601	4575	4551	4533	4516	4506	4501
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II. Band:

1. Edge:	4216.17	4215.67	4215.31	4215.04	4214.76	4214.08
	4213.71	4213.29	4212.85	4212.39	4211.90	4211.37
	4211.03	4210.82	4210.23	4209.62	4208.98	4208.29

¹ Ångström and Thalén, N. A. S. U. (1875) **9**. Deslandres, A. c. p. (1888) [6] **14**, 5, 257. Plücker, P. A. (1858) **105**, 77; (1859) **107**, 533. Watts, P. M. (1869) [4] **38**, 249; **41**, 12. Wüllner, P. A. (1872) **144**, 481. Wesendonck, W. A. (N. F.) (1881) **17**, 427. Ångström, P. A. **94**, 141. Thollon, A. c. p. (1881) [5] **25**, 287. Piazzzi-Smyth, P. T. E. **30**, 94. P. M. [4] **49**, 24. A. S. Herschell, P. T. E. **30**, 152.

² Kayser and Runge, A. B. A. 1889. Liveing and Dewar, P. R. S. **30**, 494; **33**, 403; **34**, 123. Fox-Talbot, P. M. [3] **4**, 114. Dibbitts, De Spectraal

	4207.59	4206.85	4206.08	4205.30	4204.46	4203.61
	4202.70	4202.17	4200.85	4198.85	4197.82	4197.29
2. Edge:	4197.29	4196.10	4193.08	4191.51	4190.30	4189.68
	4189.07	4185.89	4185.09	4182.44	4181.52	4181.03
3. Edge:	4178.01	4177.53	4175.04	4171.87	4167.82	
4. Edge:	4165.54	4165.24	4163.54	4161.80	4161.43	4160.01
5. Edge:	4158.22					
6. Edge:	4152.93	4149.31	4146.06	4143.12	4140.94	4140.34
	4137.44	4133.81	4133.44	4131.24	4128.19	4126.72
	4124.30	4122.35	4119.48	4114.20	4110.04	4106.78
	4102.89	4099.27	4097.04	4092.98	4090.95	4090.25
	4087.93	4083.31	4077.89	4076.06	4073.74	4069.38
	4053.40	4051.05	4034.61			

III. Band:

1. Edge:	3883.60	3880.63	3880.26	3879.90	3879.50	3879.08
	3878.65	3876.12	3874.37	3873.17	3872.93	3872.42
2. Edge:	3871.59	3870.32	3870.12	3866.18	3864.49	3863.57
	3862.69	3862.03				
3. Edge:	3861.91	3860.83	3859.85	3858.86	3857.87	3856.87
	3855.81					
4. Edge:	3855.06	3852.59	3851.46	3850.35	3849.19	3848.03
	3845.63	3845.06	3844.40	3843.17	3841.91	3840.63
	3834.00	3839.34	3838.02	3836.69	3835.34	3833.98
	3832.60	3832.01	3831.20	3830.80	3829.79	3828.36
	3826.89	3825.45	3823.95	3822.48	3821.93	3820.94
	3819.41	3817.84	3816.29	3814.72	3811.49	3809.87
	3808.53	3806.56	3804.86	3803.21	3801.48	3800.19
	3799.78	3798.05	3797.07	3796.28	3793.89	3792.75
	3792.27	3787.32	3783.65	3781.80	3779.92	3778.03
	3777.23	3776.12	3775.40	3774.21	3773.65	3772.29
	3771.92	3768.42	3764.46	3762.46	3761.13	3760.47
	3758.45	3756.45	3752.38	3746.19	3744.11	3742.00
	3739.90	3738.55	3736.62	3733.54	3731.41	3729.25
	3728.86	3727.11	3724.95	3722.78	3720.60	3720.12
	3718.42	3716.23	3714.03	3713.06	3711.85	3709.65
	3705.15	3702.96	3700.75	3698.52	3697.16	3696.28
	3694.05	3691.79	3689.55	3685.05	3682.82	3681.37

Analyse. 1863. P. A. (1864) **122**, 497. Draper, P. M. (1848) [3] **32**, 108. Morren, A. c. p. (1865) [4] **4**, 305. Plücker and Hittorf, P. T. **155**, 1. Jahresber. 1864, p. 110. A. Mitscherlich, P. A. **121**, 459. Watts, P. M. (1868) [4] **38**, 249; (1871) **41**, 12. Wüllner, P. A. (1871) **144**, 517. Lockyer, P. R. S. **27**, 308. Ciamician, Wien. Ber. 1880. Wesendonck, W. A. (N. F.) (1881) **17**, 427. A. S. Herschell, P. T. E. **30**, 154. Thalén, Le spectre du fer. 1884. Deslandres, A. c. p. (1888) [6] **14**, 5.

3680.55	3679.40	3678.30	3676.05	3673.79	3671.54
3669.78	3669.30	3667.04	3664.81	3662.57	3662.26
3658.09	3655.86	3653.66	3651.45	3648.03	3644.30
3642.67	3641.15	3640.50	3638.33	3637.31	3636.39
3635.24	3633.09	3631.65	3629.35	3624.22	3619.17
3607.92	3607.44	3606.98	3606.51	3606.05	3605.60
3605.13	3604.73	3604.27	3602.95	3597.89	3594.30
3593.86	3593.44				

IV. Band:

1. Edge: 3590.52

2. Edge: 3585.99

3, Edge:	3584.10	3583.38	3582.01	3581.76	3580.39	3580.07
	3579.26	3578.93	3578.62	3578.28	3577.23	3576.88
	3576.48	3575.73	3575.13	3574.50	3573.87	3572.60
	3571.93	3571.27	3570.59	3569.96	3569.89	3569.17
	3568.44	3567.53	3567.02	3566.93	3566.27	3564.95
	3563.96	3561.60	3561.42	3560.75	3557.34	3556.13
	3554.48	3553.72	3552.86	3549.11	3548.67	3548.36
	3545.92	3545.11	3540.53	3540.10	3537.66	3534.75
	3530.35	3528.75	3527.74	3524.70	3524.51	3523.51
	3520.01	3517.16	3512.79	3511.65	3510.38	3509.48
	3506.65	3503.83	3501.67	3497.21		

CERIUM.

The spark-spectrum of cerium is obtained by the use of the chloride. In the arc-spectrum Lockyer¹ has observed 32 additional lines between $\lambda = 3900$ and 4012 .

Spark-spectrum:

5512.2	5409.7	5393.7	5353.1	5274.2	4714.5	4629.0	4573.4
4562.9	4561.4	4540.4	4528.4	4527.4	4523.9	4460.3	4428.8
4392.2	4386.2	4382.7	4296.6	4289.6			

CHLORINE.

The line-spectrum is obtained by the passage of an electric discharge through a vacuum-tube, or through chlorine under the ordinary pressure, and also by short sparks between platinum electrodes immersed in hydrochloric acid. Hassel-

¹ P. R. S. 27, 280. P. T. 1881, 3. See also Thalén, N. A. S. U. [3] 6. Kirchhoff, A. B. A. 1861. Bunsen, P. A. 155, 366.

berg¹ observed that the chlorine-spectrum is produced by passing powerful sparks through glass tubes containing chlorine compounds under low pressure. The spectrum obtained with a powerful continuous current differs from that produced when a condenser is introduced into the circuit.²

There are no recent measurements of the absorption-spectrum of chlorine.

Spark-spectrum:

5457.8	5444.7	5425.0	5393.4	(5220.8	5217.2)	5103.2	5099.0
5078.4	4918.1	(4905.4	4897.8)	4820.8	4810.7	4794.9	

Absorption-spectrum:³ Numerous absorption-bands in the green and blue, total extinction in the violet.

CHROMIUM.

The arc-spectrum of chromium between D and $\lambda = 3430$ has been accurately measured by Hasselberg.⁴ Huggins⁵ and Thalén⁶ had previously investigated lines of the spark-spectrum in the visible region, Lockyer⁷ observed some additional lines between $\lambda = 4000$ and 3900 , and Liveing and Dewar⁸ worked on the ultra-violet portion of the arc-spectrum. Solutions of chromium compounds produce characteristic absorp-

¹ Bull. Acad. St. Pétersb. **28**, 405. See also Van der Willigen, P. A. **106**, 624. Ditte, C. r. **73**, 622. Plücker, P. A. **107**, 528. Plücker and Hittorf, P. T. **155**, 1. Ångström, C. r. **73**, 369. Thalén, K. Svenska Vetensk. Akad. Handl. **12**, No. 4, p. 8. Salet, A. c. p. [4] **28**, 24. Ciamician, Wien. Ber. **78**, 872.

² Trowbridge and Richards, Amer. Jour. Sci. (1897) [4] **3**, 117. P. M. **43**, 135.

³ Morren, P. A. (1869) **137**, 165. Sillim. Journ. [2] **47**, 417.

⁴ Svensk. Vetensk. Akad. Handl. (1894) **28**, N. 5.

⁵ P. T. (1864) **154**, 139.

⁶ N. A. S. U. [3] **6**.

⁷ P. T. 1881.

⁸ P. R. S. (1881) **32**, 402. See also H. W. Vogel, Monatsber. Berl. Akad. 1878, p. 413. Ber. **8**, 1533. Kirchhoff, A. B. A. 1861. Ångström, Recherches sur le spectre solaire. 1868. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874).

tion-spectra¹ that have been frequently studied; the more important are shown in Fig. 41, Chapter VIII. The spectroscopic determination of potassium chromate, potassium bichromate, and chrome alum is described in G. and H. Kruss' work on Colorimetry and Quantitative Spectrum Analysis.

Arc-spectrum:

5791.20	5788.15	5785.21	5784.09	5698.55	5409.99	5400.82
5348.50	5345.98	5329.30	5328.50	5300.90	5298.43	5298.14
5297.52	5296.86	5276.20	5275.85	5275.31	5265.88	5264.32
5255.27	5247.68	5225.08	5208.58	5206.20	5204.67	5196.60
4954.92	4942.63	4936.51	4922.40	4887.15	4870.96	4862.00
4829.50	4801.17	4792.61	4789.45	4756.30	4737.50	4730.88
4718.57	4708.16	4698.77	4698.60	4689.54	4666.67	4664.94
4663.98	4663.47	4652.31	4651.44	4646.33	4926.31	4622.60
4622.07	4616.28	4613.54	4600.92	4595.78	4591.56	4580.22
4571.85	4569.76	4565.71	4546.15	4544.77	4540.90	4540.70
4539.96	4535.95	4530.92	4527.53	4526.65	4512.05	4497.02
4385.11	4374.34	4373.41	4371.44	4359.78	4351.91	4351.20
4344.66	4339.85	4339.60	4289.87	4274.91	4263.28	4254.49
4163.76	4153.96	4126.67	4067.05	3991.26	3984.02	3976.81
3971.39	3969.89	3963.82	3928.79	3921.20	3919.31	3916.38
3915.96	3908.87	3903.02	3894.20	3886.94	3885.35	3883.41
3857.74	3854.36	3850.13	3841.42	3830.17	3804.91	3797.85
3749.13	3744.01	3743.67	3656.36	3649.12	3641.95	3639.93
3605.46	3593.57	3578.81	3550.73	3465.40		

COBALT.

The line-spectrum of cobalt, in the visible field, has been frequently investigated by the earlier workers. Kirchhoff,² Huggins,³ Thalén,⁴ Lecoq de Boisbaudran,⁵ and Schuster examined the spark-spectrum, and Ångström⁶ and Thalén

¹ Brewster, P. A. (1836) **37**, 315. Erhard, Inaug.-Diss. (Leipzig, 1875). Müller, P. A. (1847) **72**, 67. H. W. Vogel, Ber. (1875) **8**, 1533. Monatsber. Berl. Akad. 1878, p. 413. Stoney and Reynolds, B. A. R. 1878. Sabatier, C. R. (1886) **103**, 49. Lapraik, J. pr. Chem. 1893 [2] **47**, 305. Étard, C. r. (1895) **120**, 1057.

² A. B. A. 1861.

³ P. T. 1864, 139.

⁴ N. A. S. U. [3] **6**. From λ 3998.0 — λ 2244.8.

⁵ Spectres lumineux (Paris, 1874).

⁶ Recherches sur le spectre solaire, 1868.

that of the arc; Lockyer¹ and Cornu² have also investigated portions of the spectrum. Hasselberg³ has recently measured the lines of the arc-spectrum between D and $\lambda = 3450$, and Liveing and Dewar,⁴ those of the arc and spark spectra in the ultra-violet region. The lines of the two spectra differ not only in number, but also in intensity. The absorption-spectra of cobalt glass, and of solutions of cobalt compounds are very characteristic; they have been examined by H. W. Vogel,⁵ Russell,⁶ Russell and Orsman,⁷ and by C. H. Wolff,⁸ and are shown in Fig. 41, Chapter VIII. The following test is stated by Wolff to be one of the most delicate known in chemistry: Ammonium thiocyanate is mixed with cobalt chloride solution, and shaken with amyl alcohol and ether; this dissolves the cobalt thiocyanate, and the solution gives a characteristic absorption-spectrum. The method was used for the spectrophotometric determination of cobalt when present in small quantity. The absorption-spectrum of cobalt chloride in hydrochloric acid solution is stated by W. J. Russell to be particularly sharp, but if the acid is concentrated the broad bands usually observed are resolved into smaller ones, almost coincident with those produced by ferric chloride under the same conditions. He believes that the solvent causes a dissociation of the dissolved substance.

Arc and spark spectra:

6143.8*	6122.3*	5531.06	5525.27	5523.56	5489.90	5484.22
5483.57	5477.13	5454.79	5444.81	5407.75	5381.99	5369.79

¹ P. T. 1881. Part 3.

² Spectre normal du soleil (Paris, 1881).

³ Svenska, Vetensk. Akad. Förhandl. (1896) **28**, No. 6. From $D - \lambda 3450$. Astrophys. Jour. (1896) **3**, 288; **4**, 343; (1897) **5**, 38.

⁴ P. T. (1888) **179**, 231. From $\lambda 3450-2244$.

⁵ Ber. **11**, 916. Monatsber. Berl. Akad. 1878, p. 415.

⁶ P. R. S. **31**, 51. Ber. **14**, 503.

⁷ J. Chem. Soc. 1889, p. 14. Ber. **24**, 619.

⁸ Zeitschr. Anal. Chem. **18**, 38. See also Étard, C. r. (1895) **120**, 1057.

* Visible only in the spark-spectrum.

5362.97	5359.41	5353.69	5352.22	5343.58	5342.86	5341.53
5331.65	5325.44	5316.96	5312.84	5301.24	5280.85	5276.38
5268.72	5266.71	5266.51	5257.81	5248.12	5235.37	5230.38
5212.87	5176.27	5156.53	5154.26	5146.96	5133.65	5126.37
5125.88	5123.01	5113.41	5109.08	5095.18	4988.15	4980.15
4972.16	4966.77	4928.48	4904.37	4899.72	4882.90	4868.05
4843.61	4840.42	(4814.16	4813.67)	4796.00	4793.03	4785.26
4781.62	4780.14	4778.42	4776.49	4771.27	4768.26	4767.33
4754.59	4749.80	4737.95	4735.04	4728.14	4718.67	4698.60
4693.37	4682.53	4663.58	4657.56	4644.48	4629.47	4625.88
4623.15	4597.02	4594.75	4581.76	4580.32	4570.18	4566.77
4565.74	4549.80	4546.14	4543.99	4534.18	4531.14	4517.28
4514.33	4494.92	4484.07	4483.70	4478.45	4471.70	4469.72
4467.04	4445.88	4421.48	4417.55	4392.02	4391.70	4380.25
4375.09	4373.77	4371.27	4339.76	4331.38	4303.36	4285.93
4252.47	4234.18	4190.87	4162.33	4158.58	4121.47	4118.92
4110.69	4086.47	4082.76	4077.55	4076.28	4068.72	4066.52
4058.75	4058.36	4053.08	4045.53	4035.73	4027.21	4021.05
3998.04	3995.45	3979.65	3978.80	3974.87	3973.29	3969.25
3958.06	3953.05	3945.47	3941.87	3911.01	3936.12	3922.88
3917.26	3910.08	3906.42	3895.12	3894.21	3884.76	3882.04
3876.99	3874.10	3873.25	3861.29	3851.09	3845.95	3842.20
3816.58	3816.46	3755.59	3750.06	3745.61	3736.05	3734.30
3733.62	3732.52	3730.61	3708.96	3702.40	3693.65	3693.27
3684.62	3683.18	3676.69	3652.68	3649.47	3647.82	3643.34
3641.95	3639.63	3634.86	3633.00	3631.55	3627.96	3625.13
3611.89	3605.50	3595.00	3587.30	3585.28	3584.92	3575.48
3575.06	3569.48	3565.08	3563.04	3562.22	3561.01	3558.90
(3553.12	3552.85)	3550.72	3548.60	3543.40	3533.49	3529.92
3529.17	3526.96	3523.85	3523.57	3521.70	3520.20	3518.49
3513.62	3512.78	3510.53	3509.98	3506.44	3502.76	3502.41
3496.83	3495.82	3491.46	3490.89	3489.54	3485.49	3483.55
3474.15	3471.52	3466.0	3462.9	3453.6	3449.3	3443.7
(3434.0	3433.5)	3432.0	(3413.7	3413.4	3410.3	3406.0
3396.5	3389.3	3388.8	3381.7	3368.3	3356.4	3336.1)
3284.9	3158.6	3154.6	3147.0	3139.9	3137.4	3121.5
3086.7	3082.5	3072.4	3061.9	3049.0	3044.0	2989.5
2986.9	2954.5*	2942.9	2824.9	2648.8	2580.2	2564.0
2541.9	2540.6	2533.8*	2532.1	2530.0	2528.5	2524.9*
2524.6	2521.1	2519.7*	2510.9	2506.2	2497.5	2490.2
2464.1	2436.9	2432.4	2420.7	2417.6	2411.6	2407.5
2397.3	2388.8	2378.5	2363.7	2353.4	2313.9	2311.5
2307.8	2293.4	2286.1	2266.6*	2260.1*	2256.8*	2245.2*

* Visible only in the spark-spectrum.

COPPER.

The spark-spectrum of copper, in the visible field, has been measured by Kirchhoff,¹ and Thalén,² and, as far as wavelength 4275, by Lecoq de Boisbaudran;³ in the ultra-violet Hartley and Adeney⁴ have measured the portion between $\lambda = 3999$ and 2103 , and Trowbridge and Sabine⁵ that between $\lambda = 2369$ and 1944 . Liveing and Dewar⁶ have photographed the arc-spectrum from $\lambda = 2294$ – 2135 , whilst, more recently, Kayser and Runge⁷ have done the same for the region between $\lambda = 6000$ and 1944 ; they measured 304 lines, and obtained the spectrum by substituting, for the carbon poles, rods of copper 1–2 sq. cm. in section.

Scarcely any of the copper lines are sharply defined even on one side, so that the spectrum has a peculiar appearance. In the Bunsen flame cupric chloride produces a band-spectrum extending over the whole field, with the exception of the violet; the same spectrum is obtained with the metal if the flame contains hydrogen chloride. The absorption-spectra of copper salts are not characteristic, as the compounds produce total extinction both in the red and the violet. Ewan⁸ found that, in aqueous solution, the spectra of the chloride, sulphate, and nitrate change with progressive dilution tending to become identical; this observation is in agreement with the theory of electrolytic dissociation. C. H. Wolff⁹ has suggested a spectro-colorimetric method for the determination of

¹ A. B. A. 1861.

² N. A. S. U. (1868) 6.

³ Spectres lumineux (Paris, 1874).

⁴ P. T. (1883) 175, 63.

⁵ Proc. Amer. Academy, 1888. P. M. [5] 26, 342.

⁶ P. R. S. (1879) 24, 402. P. T. (1883) 174, 205.

⁷ A. B. A. 1892.

⁸ P. M. 1892, p. 317. Ber. 25, 495c. P. R. S. (1895) 57, 128.

⁹ Zeitschr. anal. Chem. 18, 38.

copper in small quantity, and P. Sabatier¹ has studied the absorption-spectra of solutions of cupric bromide.

Arc and spark spectra:

5782.30	5700.39	5292.75	5220.25	5218.45	5153.33	5105.75
4704.77	4674.98	4651.31	4587.19	4539.98	4531.04	4507.62
4480.59	4415.79	4378.40	4275.32	4259.63	4062.94	4022.83
3602.11	3599.20	3512.19	3450.47	3308.10	3290.62	3274.06
3247.65	3126.22	3108.64	3063.50	3036.17	2961.25	2766.50
2618.46	2492.22	2441.72	2406.82	2392.71	2370.5*	2369.97
2303.18	2293.92	2263.20	2230.16	2227.85	2225.77	2214.68
2199.77	2178.97	2165.20	2104.88	2025.14	1943.88	

CUPRIC CHLORIDE.²

Flame-spectrum:

6619 b	6268 b ^v	6151 b ^v	6051 b ^v	5564 b	5507	5440	5386
5306 b	5270 b	5240	5088 b ^v	5050 b ^v	4984 b ^v	4946 b ^v	4883 b ^v
4848 b ^v	4793 b ^v	4580 b ^v	4523 b ^v	4497 b ^v	4437 b ^v	4413 b ^v	4354 b ^v
4332 b ^v	4282 b ^v	4261 b ^v					

DIDYMIUM.³

The metals of the rare earths have been frequently investigated during the past few years, and new substances have been discovered in bodies which were formerly believed to be elementary. In 1885 didymium was resolved into neodymium and praseodymium, and samarium, which was discovered in 1879, was also shown to be present. Other members of the cerium and yttrium groups have likewise been decomposed into its elements. At present the chemical properties of these

¹ C. r. **118**, 1042, 1144. Ber. **27**, 489, 490. See also Glan. W. A. (1878) **3**, 65. Krüss. Colorimetrie (Hamburg, 1891).

² Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Diacon, A. c. p. (1865) [4] **6**, 5. A. Mitscherlich, P. A. **116**, 499; (1853) **121**, 459.

³ Thalén, Om Spectra tillhöranda Yttrium, Erbium, Didym och Lanthan (Stockholm, 1878). Öfersigt K. Vetenskaps Akad. Förhandl. (1883) **40**, No. 7. Gladstone, J. Chem. Soc. **10**, 219. Bunsen, P. A. **155**, 366. Kirchhoff, A. B. A. 1861. Delafontaine, P. A. **124**, 635. Lockyer, P. T. 1881.

* Visible only in the spark-spectrum. (Hartley and Adeney.)

substances have not been sufficiently studied to render their recognition as elements absolutely free from doubt. Krüss and Nilson, as the result of their investigation of the absorption-spectra, consider that didymium, erbium, holmium, samarium, and thulium are composed of more than twenty elements; their conclusion is based on the assumption that each element has a characteristic maximum of absorption, but Schottländer's extensive investigations show that this is fallacious. Bailey has also raised objections to Krüss and Nilson's conclusions. At present the results of the spectroscopic work on the rare earths is so uncertain, that the data given in this book usually refer to the "old" elements. Bahr and Bunsen found that didymium oxide, like erbium oxide, when heated in the Bunsen flame gives a continuous spectrum, and also characteristic bright lines which are almost coincident with the absorption-lines exhibited by solutions of the salts, or by glass which contains the metal; this is no exception to the rule that solids only yield continuous spectra, for Huggins and Reynolds showed that the earths are volatile in the oxy-hydrogen flame. Comparison of the absorption-spectra of didymium chloride, sulphate, and acetate led Bunsen to the conclusion that the bands tend to approach the red as the molecular weight increases. The absorption-spectra of the rare earths in the ultraviolet has been investigated by Soret.

Spark-spectrum:

5486.0*	5372.0	5361.5	5319.9	5293.5	5273.5	5249.5
5192.5	5191.5	5130.3	4924.5	4463.2	4452.3	4446.7
4328.1	4303.6	4109.8	4060.7			

* Due possibly to samarium.

DIDYMIUM CHLORIDE.

Absorption-spectrum:¹

b (7431.7*	7361.7*	7308.7*)	6895.6*	6793.3*	[α] b (5963†
5886†	5824*	5789*	5748*	5720)	[β] b (5313*
5206)	(5125.8*	5088*)	4823†	4759	4692†
4441.7					

“OLD” DIDYMIUM NITRATE.

Absorption-spectrum: positions of minimum of brightness:

7291	6906	6794	6407	6235	6189	5797	5759	5317
5253	5217	5147	5126	4826	4771	4695	4633	4443
4341	4289.6	4173.6						

PRASEODYMIUM NITRATE.

7291	6794	5916	5797	5759	5317	5217	5125	4826	4695	4443
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ERBIUM.²

The remarks on didymium apply also to this element.

Spark-spectrum:

5827	5763	5344.4	5257	5218	5189	4952
4899.9	4872.4	4820	4674.9	4606.3	4501.3	

¹ Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). C. r. (1887) 105, 276. Bunsen, P. A. 155, 366. Ann. Chem. Pharm. 128, 100; 131, 255. Huggins and Reynolds, P. R. S. 18, 546. Lippich, Sillim. Journ. (1873) [3] 13, 304. Auer v. Welsbach, Sitzungsber. Wien. Akad. (1885) 92. Crookes, C. N. 54, 27. Schuster and Bailey, B. A. R. 1883. H. Becquerel, C. r. 104, 777, 1691; 106, 106. Haitinger, Monatsch. f. Chem. (1891) 12, 362. Soret, C. r. 86, 1062; 88, 422; 91, 378. Krüss and Nilson, Ber. 20, 2143. Bailey, Ber. (1887) 20, 2769, 3325. Schottländer, Ber. (1892) 25, 569.

² Thalén, Om Spectra Yttrium, Erbium, Didym och Lanthan (Stockholm, 1874). Öfversigt K. Vetensk. Akad. Förhandl. (1881) 40. Bunsen and Bahr, Ann. Chem. Pharm. 137, 1. Huggins, P. R. S. 1870. Bunsen, P. A. 155, 366.

* Neodymium.

† Praseodymium.

ERBIUM CHLORIDE.¹

Absorption-spectrum:

6839	6671	6535	6405	5410
5364	[α] 5232	4922	4875	4516

FLUORINE.

There are no accurate measurements of the spectrum of fluorine. By the passage of induction-sparks through silicon fluoride Salet² obtained a beautiful blue band-spectrum of the compound; the incision of a Leyden jar produced the spark-spectrum of fluorine. Commencing at Salet's last lines Liveing³ measured the flame-spectrum.

Spark-spectrum:

6922*	6862*	6782*	6401	6231
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Flame-spectrum:

6231	6091	6011	5571	5321
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GALLIUM.

Lecoq de Boisbaudran,⁴ who discovered this element, measured its spark-spectrum, and Liveing and Dewar⁵ that of the arc.

Spark and arc spectra:

4171	4031
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GERMANIUM.

The spark-spectrum of germanium has been investigated by Kobb,⁶ and by Lecoq de Boisbaudran,⁷ who calculated its

¹ Lecoq de Boisbaudran, *Spectres lumineux* (Paris, 1874). Bunsen, P. A. **155**, 366. Bunsen and Bahr, *Ann. Chem. Pharm.* **137**, 1.

² A. c. p. (1873) **28**, 34.

³ *Proc. Cambridge Phil. Soc.* **3**, Pt. 3. See also Mitscherlich, P. A. **121**, 476. Seguin, C. r. (1862) **54**, 933.

⁴ C. r. **82**, 168.

⁵ P. R. S. **28**, 482.

⁶ W. A. (1886) **29**, 670.

⁷ C. r. (1886) **102**, 1291. Ber. **19**, 479.

* Only approximate.

atomic weight from his measurements. Rowland and Tatnall¹ have recently photographed the arc-spectrum between $\lambda = 2300-4600$.

Arc and spark spectra:

6337	6021	5893	5256.5	5229.5	5210	5178.5	5135
5131	4814	4743	4685.3	4291.6	4261	4226	4179
3269.628*	3124.945*	3039.198*	2754.698*	2740.535*	2709.734*		
2691.446*	(2651.709*	2651.219†)	2592.636*	2417.450*			

GOLD.

Living and Dewar² measured three lines in the ultra-violet exhibited by the arc-spectrum, and these were the only ones known when Kayser and Runge³ commenced their investigation of the region between wave-length 6600 and 2280. They usually employed fine gold, but occasionally auric chloride and carbon poles. The visible portion of the spark-spectrum has been measured by Kirchhoff,⁴ Huggins,⁵ Thalén,⁶ and G. Krüss,⁷ who ascribes the line 5230.47 to platinum, and not to gold.

Arc and spark spectra:

6278.37	5957.24	5837.64	5656.00	5230.47	5064.75	4792.79
4488.46	4065.22	3122.88	3033.38	3029.32	2932.33	2905.98
2676.05	2428.06					

HELIUM.

The yellow D_2 -line of the solar spectrum was ascribed, until recently, to a hypothetical element, termed by Frank-

¹ Astrophys. Jour. (1895) **1**, 149.

² P. T. (1882) **174**, 2219.

³ A. B. A. 1892.

⁴ *Ibid.* 1861.

⁵ P. T. 1864, p. 139.

⁶ N. A. S. U. [3] **6**.

⁷ Lieb. Ann. (1887) **238**, 30. See also Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874).

* Arc-spectrum.

† Possibly a single reversed line.

land helium; this was isolated by Ramsay¹ in 1895 from clèveite, in which it occurs together with argon; he also obtained it from certain meteorites from Augusta Co., Virginia. Clève² showed that it is present, unaccompanied by argon, in clèveite from Carlshuus in Norway, and he observed the presence in its spectrum of five lines in addition to D_3 . Deslandres,³ using a very high dispersion, measured the following lines:

6678	5876.0	5048.4	5016.0	4922.2	4713.35	4471.75
4437.9	4388.4	4143.9	4120.9	4026.2	3964.0	3888.75
3819.7	3705.4	3613.8	3447.7	3187.9	2945.7	

Runge and Paschen,⁴ in the course of an investigation of the gases from clèveite, showed that the line at 5876.0 is a double one, and, as the solar helium line had always been regarded as single, doubt was cast on the identity of solar and terrestrial helium. This point was speedily settled by Huggins and Hale,⁵ who showed that the solar D_3 -line is also double. Kayser⁶ found that a Geissler tube containing what he supposed to be the purest atmospheric argon also showed the D_3 -line, thus affording proof that helium is present in the atmosphere. Lockyer⁷ states that many of the helium lines coincide with some of hitherto unknown origin in the spectra of the chromosphere, and of the white stars of Orion. Under the influence of the silent discharge helium combines with mercury and benzene or carbon bisulphide to form a compound resembling that of argon, but it does not combine with mercury alone.

¹ C. r. **120**, 660, 1049. Ber. **28**, 318, 448. N. **52**, 224. Ramsay, Collie, and Travers, Jour. Chem. Socy. (1895) **67**, 648.

² C. r. **120**, 834. Ber. **28**, 373.

³ C. r. (1895) **120**, 1110, 1331.

⁴ W. A. Beibl. **19**, 634.

⁵ C. N. **72**, 26.

⁶ *Ibid.* **72**, 99.

⁷ C. r. **120**, 1103. P. R. S. **58**, 67. See also Brauner, C. N. **71**, 271. Palmieri, Acad. di Napoli Rendic. (1882) **20**, 233.

Berthelot¹ and Runge and Paschen² have observed that the spectrum of clèveite gas consists of six series, two pairs of which are characterized as subseries, whilst two series are principal series. Two spectra are thus differentiated which are ascribed to two constituents of the gas, and which bear a striking similarity to the spectra of the alkalies. Rydberg³ has confirmed these conclusions, and termed the second constituent parhelium. Some confirmation was also afforded to this view by Ramsay and Collie's researches, which resulted in the separation of helium into a lighter and a heavier portion; but Ames and Humphreys⁴ were unable to detect any difference in their spectra, although they used a spectroscope of high dispersive power. When further separated the heavier portion was found to consist chiefly of argon.

HYDROGEN.

Two spectra, termed the *elementary* and *compound* line-spectra, are exhibited by hydrogen in a Geissler tube; their production depends on the conditions of temperature and pressure. The former has been measured by Angström,⁵ H. W. Vogel,⁶ Lockyer,⁷ Huggins,⁸ Cornu and Ames;⁹ the latter was first investigated by Plücker and Hittorf,¹⁰ but was ascribed to acetylene by Ångström, Berthelot and Richard,¹¹ and Salet.¹² The incorrectness of this view was proved by

¹ C. r. (1897) **124**, 113.

² Sitzber. Berl. Akad. (1895) 639, 759. W. A. Beibl. (1895) **19**, 884, 885. Astrophys. Jour. (1896) **3**, 4.

³ W. A. (1896) **58**, 674. Astrophys. Jour. (1896) **4**, 91.

⁴ Astrophys. Jour. (1897) **5**, 97.

⁵ P. A. (1864) **91**, 141; **123**, 489; (1872) **144**, 300.

⁶ Berl. Monatsber. (1879) 586; (1880) 190. Ber. (1880) **13**, 274.

⁷ P. R. S. **28**, 157; **30**, 31.

⁸ P. T. **171**, 669.

⁹ P. M. (1890) [5] **30**, 33.

¹⁰ P. T. (1865) **155**, 21. Plücker, P. A. **107**, 497.

¹¹ C. R. **68**, 810, 1035, 1107, 1546.

¹² A. c. p. [4] **28**, 17.

Hasselberg's¹ exact measurements. In the spectrum of ζ Puppis Pickering² found, in addition to dark hydrogen lines and K , two broad lines at $\lambda = 4633$ and $\lambda = 4688$, and a peculiar series of dark lines whose wave-lengths are rhythmically related. These were $\lambda = 4544, 4201, 4027, 3925, 3859, 3816, 3783$. It was first thought that they represented some new element not yet found on the earth or in the stars, but they are very probably due to hydrogen, produced under conditions of luminosity hitherto unknown. By applying Balmer's formula, Pickering found that the new lines form a harmonic series. This conclusion was confirmed by Kayser,³ who pointed out that hydrogen had been the only element, having harmonically related lines, which had possessed only a single series of such lines. Kayser and Runge had previously found that two of the series of lines of an element end at nearly the same place. On examining the oscillation frequencies of the new lines, Kayser concluded that they have this characteristic, and constitute a new hydrogen series. If these lines can be produced in laboratory experiments, important information as to stellar temperatures and pressures is likely to be obtained.

At low temperatures *water vapor* gives an absorption-spectrum rich in lines which are chiefly confined to the red region; these constitute a large number of the terrestrial Fraunhofer lines, and are referred to under nitrogen; they are strongest when the sun is low in the horizon, as its rays have then to traverse a considerable layer of the atmosphere. When the latter is saturated with moisture, a "rain-band" is visible with the help of a spectroscope of low dispersive

¹ Bull. Acad. St. Pétersb. (1880) **11**, 307; (1884) **12**, 203. Mém. Acad. St. Pétersb. (1882) **30**, No. 7; (1883) **31**, No. 14. W. A. **15**, 45. See also H. C. Vogel, P. A. (1872) **146**, 569. Wüllner, P. A. **135**, 497; **137**, 337; **144**, 481. W. A. **14**, 355. Seabroke, P. M. [4] **43**, 155. Balmer, W. A. (1885) **25**, 80.

² Astrophys. J. (1897) **5**, 92. Science (1897) **5**, 726.

³ Astrophys. J. (1897) **5**, 95. Science (1897) **5**, 726.

power: it consists of bands composed of water-vapor lines, and situated between the red end and the *D*-line. The presence of the rain-band has been used by Piazzzi-Smyth,¹ Capron,² Grace and others as a means of prognosticating rain.

Janssen³ investigated the absorption-spectrum of steam contained in long tubes under considerable pressure, and Schön⁴ states that pure water exhibits an absorption-band. An emission-spectrum consisting of numerous lines in the ultra-violet is obtained by burning hydrogen in air, or passing it through the electric arc; it has been measured by Huggins, and also by Liveing and Dewar,⁶ who distinguished five series of lines. The first, between wave-length 3268.2 and 3063.7, contains about 116 lines; the second, from 3057 to 2812, comprises 180 lines; the third, from 2807 to 2609, contains 141 lines; the fourth series, from 2606 to 2450, has 88 lines; and the fifth series includes 79 lines between wave-length 2449 and 2268.

Elementary line-spectrum:

[C or H α] 6563.04	[F or H β] 4861.49	[G or H γ] 4340.66	[h or H δ] 4101.85
[H] 3970.25	[α] 3889.15	[β] 3835.6	[γ] 3798.0
[δ] 3770.7	[ϵ] 3752.05	[ζ] 3734.15	[η] 3721.8
[θ] 3711.9 (Ames).			

Compound line-spectrum:

6135.5	6121.9	6081.0	6070.7	6032.1	6018.5	5975.8
5938.9	5931.8	5888.9	5884.5	5813.0	5084.9	5055.2
5013.15	4973.3	4934.5	4928.8	4861.49	4719.2	4683.95

¹ N. 26, 551.

² The Observatory, 1882, pp. 42, 71.

³ C. r. 63, 289.

⁴ P. A. Suppl. Bd. (1878) 9, 670. W. A. 6, 267. See also for the *spectrum of water* Huggins, P. R. S. 30, 576. C. r. (1872) 74, 1050. Liveing and Dewar, P. R. S. 30, 580; 33, 274. P. T. (1888) 179, 2. Lecoq de Boisbaudran, C. r. 74, 1050. Deslandres, A. c. p. (1888) [6] 14, 257. C. r. 100, 854. *Absorption spectrum*, Janssen, C. r. 54, 1280; 56, 538; 60, 213. Russell and Lapraik, N. (1880) 22, 368. Soret and Sarasin, Arch. Sc. phys. et nat. (1884) 11, 327. C. r. 98, 624. Ewan, P. R. S. (1895) 57, 126.

⁶ P. R. S. 35, 74.

4634.15	4461.1	4412.35	4340 66	4212.65	4205.2	4195.9
4177.25	4171.35	4101.85	4079.0	4069.75	4067.0	4062.6
3990.15	3970.25	3889.15	3871.8	3863.3	3835.6	3804.9
3796.8	3684.3	3674.5 (Hasselberg, Ames).				

INDIUM.

This element was discovered in 1864 by Reich and Richter¹ by means of its flame-spectrum, which consists of an indigo-blue and a violet line. The visible portion of the spark-spectrum has been measured by Clayden and Heycock,² and a small part of it also by Thalén,³ whilst Hartley and Adeney⁴ investigated the ultra-violet region. The arc-spectrum has been examined by Liveing and Dewar;⁵ it contains only the two lines above mentioned, which were accurately measured by Kayser and Runge.⁶ Indium furnishes a remarkable example of the simplicity of the arc-spectrum as compared with that of the spark; the latter contains numerous lines both in the visible and ultra-violet regions which are absent from the former.

Flame-spectrum⁷:

4511.44 4101.87

Arc-spectrum:

4511.44	4101.87	3258.66	3256.17	303946.
2932.71	2753.97	2714.05	2710.38	2601.84
2560.25	2521.45	2460.14	2389.64	2340.30

Spark-spectrum:

6907.6	6193.9	6096.0	5821.0	5645.0	5251.0	4680.9
4656.9	4638.8	4532.8	4511.44	4253.7	4101.87	4072.3
4064.2	4033.4	3853.5	3835.3	3258.66	3256.17	3039.46
2932.71	2890.2	2710.38	2560.25	2527.5	2521.45	2460.14
2389.64	2351.7	2306.8				

¹ J. pr. Chem. 89, 441.

² P. M. (1876) 5, 387.

³ N. A. S. U. (1868) [3] 6.

⁴ P. T. (1883) 175, 63.

⁵ P. R. S. (1879) 28, 367.

⁶ A. B. A. 1892.

⁷ Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Müller, P. A. 124, 637.

IODINE.

The more important investigations of the line-spectrum of iodine are those of Plücker and Hittorf,¹ and of Salet;² the latter passed sparks from Leyden jars, or a Holtz machine, through a Geissler tube containing iodine: the tube was not closed until the iodine vaporized. There are no new determinations. The spectrum obtained with a condenser in the circuit differs from that produced by the continuous discharge.³ The violet iodine vapors produce an absorption-spectrum extending over the red and green, but not over the blue and violet regions; it consists of numerous slender lines grouped into bands, and has been accurately measured by Hasselberg.⁴ H. W. Vogel⁵ has examined the absorption-spectra of various solutions of iodine, whilst Gernez⁶ has studied those of iodine chloride and iodine bromide. The rule that the coefficient of extinction of solutions of a colored substance changes with the concentration, is found by E. Thiele⁷ not to apply to iodine; he investigated the absorption-spectrum of solutions of varying strength in the same solvent. Previous exceptions to this rule had all been electrolytes, and their abnormal behavior had been thought to be due to electrolytic dissociation, but iodine is a non-electrolyte.

¹ P. T. 155, 24.

² Spectroscopie (Paris, 1888). C. r. 74, 1249; 75, 76. A. c. p. [4] 28, 29. See also Plücker, P. A. (1859) 107, 638. Ciamician, Wien. Ber. [2] 78, 877. Wüllner, P. A. 120, 158. Mitscherlich, P. A. 121, 474.

³ Trowbridge and Richards, Amer. Jour. Sci. (1897) [4] 3, 117. P. M. 43, 135.

⁴ Mém. de l'Acad. St. Pétersb. (1888) [7] 36. See also Daniell and Miller, P. A. 28, 386. Morghen, Beiblätter, 8, 822. Thalén, Le spectre d'Absorption de la vapeur d'Iode (Upsal, 1869).

⁵ Ber. 11, 919. Monatsber. Berl. Akad. 1878, p. 417.

⁶ C. r. 74, 466.

⁷ Zeitschr. phys. Chem. 16, 147. Ber. 28, R 720.

Spark-spectrum:

6258	6211	6126	6079	5953	(5791	5774	5761	5739	5712)
(5689	5674)	5625	(5495	5462	5534	5404)	(5345	5337)	5244
5163	5016	4866	(4678	4669)	4634				

Absorption-spectrum of iodine vapor:

Group 6316—6272 :	6316.51	6298.29	6297.76	6294.75	6294.25
	6291.94	6291.46	6289.83	6272.42	
Group 6272—6234 :	6253.07	6252.96	6237.72		
Group 6234—6191 :	6233.93	6229.68	6212.41	6210.18	6191.87
Group 6191—6149 :	6190.97	6153.08	6149.48		
Group 6149—6111 :	6111.25				
Group 6111—6069 :	6108.87	6069.31			
Group 6069—6031 :	6063.49	6047.82	6046.87	6045.94	6042.81
	6035.82	6034.83	b (6033.40	6033.05)	b (6031.92
	6031.58)				
Group 6031—5992 :	6030.99	6024.38	6020.38	6018.37	6008.85
	(5994.65	5994.42)	5993.89	5993.03	
Group 5992—5976 :					
Group 5955—5917 :	(5948.83	5948.62)	b (5922.53	5922.04)	b (5921.77
	5921.24)	b (5921.00	5920.58)	5920.00	5919.75
	5919.36	5919.11	5917.55		
Group 5917—5881 :	5885.00	5884.74	5884.10	5881.17	
Group 5881—5846 :	5866.91	5859.85	5856.49	(5850.51	5850.22)
	5848.57	5847.08	5846.54	5846.22	
Group 5846—5811 :	5815.40	5812.66	5811.65		
Group 5811—5778 :	(5805.86	5805.63)	(5798.69	5798.45)	(5798.14
	5797.93)	5793.47	5778.87	5778.62	5778.28
Group 5778—5746 :	5746.21				
Group 5746—5715 :	5745.92	5720.60	5715.45		
Group 5715—5684 :	5714.92	5712.24	5708.38	5698.70	5697.84
	5693.05	5685.09	5684.54		
Group 5684—5655 :	5683.08	5678.59	5676.82	5658.98	
Group 5655—5626 :	5654.71	5649.61	5647.68	5646.72	b (5646.14
	5645.50)	5640.90	5640.00	5639.15	b (5638.64
	5638.23)	5637.36	(5628.90	5628.35)	5627.97
	5627.19	5626.50			
Group 5626—5599 :	(5620.59	5620.33)	5616.50	5614.53	5602.98
	5601.81	5699.14			
Group 5599—5587 :	5588.98	5587.56			
Group 5587—5560 :	5585.10	(5577.63	5577.42)	5574.11	5572.71
	5561.58	5560.44	5560.25	5559.57	
Group 5560—5533 :	5557.17	5553.61	5549.40	b (5547.92	5546.96
	5546.07)	5545.57	5542.37	5540.91	5533.37

Group 5533—5507 :	b(5531.75 5521.79)	5531.10 5521.34	5527.58 5520.33	5526.38	b(5522.25)
Group 5507—5482 :	5505.19 (5497.51 5488.95	5504.95 5497.15)	5500.43 5496.36 5482.11)	5498.32 5490.37	5497.81 5489.67
Group 5482—5457 :	5473.55 (5457.90	b(5483.00 5473.12 5457.08)	5472.67)	5468.38	5466.76
Group 5457—5434 :	5438.43	5434.03			
Group 5434—5411 :	5430.71 5414.28	5425.76 5412.31	5419.78 5411.66	5418.85	5416.99
Group 5411—5389 :	b(5410.75 5390.85	5404.96 b(5390.21	5404.04 5389.01)	b(5393.91	5393.44)
Group 5389—5367 :	5381.90 5374.38	5380.93 5369.74	5378.05 5369.20	5377.32 5368.51	5375.20 5368.01
Group 5367—5347 :	5364.76 5353.28	5358.81 5350.56	5357.91 5349.87	5356.63 5348.06	5355.89 5347.35
Group 5347—5327 :	5346.24 5333.10	5343.12 5330.97	5341.43 5329.32	5340.14	5333.73
Group 5327—5308 :					
Group 5308—5291 :					
Group 5291—5273 :	5290.72				
Group 5273—5255 :	5272.75				
Group 5255—5240 :					
Group 5240—5224 :	5224.10				
Group 5224—5209 :	5215.83	5209.46			
Group 5209—5195 :	5195.22				
Group 5195—5182 :					
Group 5182—5168 :	5181.96	5168.65			
Group 5168—5156 :	5161.45	5156.16			
Group 5156—5145 :	5144.71				

IRIDIUM.

There are no accurate measurements of the spectrum of this element. Kirchhoff¹ observed three faint lines of $w-l$, 6348.1, 5450.6, and 5300.6, and Lockyer² has measured six in the arc-spectrum between wave-length 4000 and 3900. H. W. Vogel³ has described the absorption-spectrum of ammonium iridio-chloride.

Arc-spectrum:

3992.2	3976.0	3945.8	3934.7	3915.2	3902.5
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¹ A. B. A. 1861.² P. T. 1881, Pt. 3.³ Prakt. Spectralanal. (Berlin, 1889).

IRON.

The spectrum of iron is the richest in lines; they are distributed over every part of the field, and therefore, like the Fraunhofer lines, are excellently adapted for purposes of orientation in spectroscopic observations. Omitting the older and less accurate measurements, the following investigations are of greatest importance: Thalén¹ made a careful comparison of the lines in the iron-carbon arc with those of the solar spectrum shown in the atlases of Ångström, and of Fiévez and Vogel, and investigated those between $760\mu\mu$ and $400\mu\mu$. In the ultra-violet Cornu² photographed the more prominent lines between $410\mu\mu$ and $295\mu\mu$, and Liveing and Dewar³ carefully extended this work to the region between $295\mu\mu$ and $230\mu\mu$; they also, as did Hartley and Adeney,⁴ investigated the spark-spectrum of iron. All these measurements were based on Ångström's erroneous determination of the wave-length of the *D*-line, so that a reinvestigation of the subject was very desirable. Kayser and Runge⁵ undertook this task, and usually attained an accuracy of 0.02 Ångströms; they measured more than 4500 lines, and on comparing them with Rowland's solar atlas between $520\mu\mu$ and $320\mu\mu$, they were unable with certainty to detect a single line which does not appear in the solar-spectrum. The absorption-spectra of solutions of various compounds of iron are not specially characteristic; they have been studied by

¹ N. A. S. U. [3] 6. Le spectre du fer. 1884.

² Spectre normal du soleil (Paris, 1881).

³ P. T. 174, 210. P. R. S. 32, 402.

⁴ P. T. 1884.

⁵ A. B. A. 1888, 1890. See also Huggins, P. T. (1864) 154, 139. Kirchhoff, A. B. A. 1861. Ångström, Recherches sur le spectre solaire, 1868. Mascart, Ann. de l'école normale (1866), 4. Secchi, C. r. (1873) 77, 173. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Lockyer, P. T. 164, 479. H. W. Vogel, Prakt. Spectralanal. (Berlin, 1889).

H. W. Vogel,¹ and are referred to in the following chapter. Roscoe,² Lielegg,³ Marshall Watts,⁴ and others have investigated the spectrum of the flame observed during the manufacture of steel by the Bessemer process, and more recently it has been thoroughly examined by Hartley.⁵ Watts believed that the green bands are produced by manganese oxide, and that their disappearance marks the instant when the iron is completely decarbonized, and the blast of air should be stopped. Before the application of the spectroscope for this purpose it was exceedingly difficult to determine the precise moment, since experience was the sole guide and often proved untrustworthy.

Hartley's exact investigations have shown that the phenomena of the Bessemer flame is much more complex than was previously divined. This is owing to the superposition of bands of manganese, carbon, carbonic oxide, and possibly also of those of manganese oxide, and of the lines of iron, manganese, potassium, sodium, lithium, and hydrogen. The bands of manganese are to some extent obscured by the strong continuous spectrum of the carbonic oxide flame, and by the bands of carbon.

The cause of the nonappearance of the lines in the spectrum at the beginning of the "blow" is the comparatively low temperature at this period, and the free oxygen, which escapes with carbon dioxide, giving a gaseous mixture con-

¹ Ber. (1875) **8**, 1537. See also Müller, P. A. (1847) **72**, 67. Ewan, P. R. S. (1895) **57**, 140.

² P. M. P. S. 1863.

³ Sitzungsber. Wien. Akad. 1867.

⁴ P. M. [4] **34**, 437; **38**, 249.

⁵ P. T. (1894) **185**, 1041. P. R. S. (1895) **59**, 98. Journ. Iron and Steel Inst. (1895) No. II. See also Kohn, Dingler polyt. J. (1864) **175**, 296. Silliman, P. M. **41**, 1. Tunner, Dingler polyt. J. (1865) **178**, 465. Brunner, Oester. Zeitschr. für Berg- und Hüttenwesen (1868), **16**, 226. Kuppelwieser, *Ibid.* (1868) **16**, 59. v. Lichtenfels, Dingl. polyt. J. **191**, 213. Spear Parker, C. N. **23**, 25. Wedding, Zeitschr. f. Berg-, Hütten- und Salinenwesen (1869), **27**, 117. Greiner, Revue universelle (1874), **35**, 623.

taining too small a proportion of carbonic oxide to produce luminosity. During the "boil" the luminosity of the flame is due to the combustion of highly heated carbonic oxide, and also to the presence of the vapors of iron and manganese. The disappearance of the manganese-spectrum at the end of the "fining" stage is primarily caused by the carbonic oxide, which escapes from the converter, being reduced in quantity owing to the diminished supply of carbon in the metal. When the last traces of carbon are gone, so that air can escape through the metal, the blast instantly oxidizes any manganese, either in the metal or in the atmosphere of the converter, and also some of the iron. The temperature must then fall with great rapidity.

Arc-spectrum:

6678.23	6663.38	6633.92	6609.35	6594.11	6593.14
6575.17	6569.46	6546.47	6518.62	6495.20	6431.06
6421.55	6420.17	6411.86	6408.23	6400.27	6393.81
6380.95	6337.07	6335.55	6322.91	6318.22	6302.73
6301.71	6297.99	6291.18	6270.44	6265.34	6256.57
6254.45	6252.76	6246.53	6232.90	6230.94	6219.49
6215.36	6213.63	6200.53	6191.77	6180.42	6170.69
6157.96	6141.93	6137.91	6136.85	6128.11	6103.45
6102.40	6078.71	6065.71	6056.21	6042.31	6027.27
6024.28	6020.35	6008.78	6003.28	5987.29	5985.04
5983.98	5977.12	5975.58	5956.92	5953.01	5934.83
5930.29	5916.47	5914.38	5905.94	5862.58	5859.91
5816.59	5782.35	5775.30	5763.22	5753.33	5731.98
5718.10	5709.61	5701.77	5686.66	5662.75	5659.06
5638.52	5624.77	5615.88	5603.17	5586.99	5576.32
5573.07	5569.85	5565.83	5555.03	5506.98	5501.69
5497.70	5476.89	5474.13	5463.49	5455.83	5447.16
5445.28	5434.74	5429.81	5424.23	5415.42	5411.20
5405.99	5404.42	5400.67	5397.32	5393.38	5383.58
5371.67	5370.17	5367.67	5365.08	5353.50	5341.21
5340.16	5333.09	5328.71	5328.21	5324.37	5307.54
5302.52	5283.80	5281.97	5273.55	5270.52 [E ₂]	5269.72
5266.73	5263.42	5250.81	5242.66	5233.12	5230.01
5227.39	5227.08	5216.43	5208.80	5202.48	5195.09
5192.53	5191.68	5171.78	5169.07	5167.57	5162.45
5153.34	5151.02	5148.42	5139.65	5139.44	5137.56
5133.70	5125.30	5123.88	5110.57	5107.82	5105.73

5098.83	5083.50	5079.91	5079.42	5068.95	5065.15
5051.78	5050.01	5041.91	5015.13	5012.21	5006.30
5005.90	5002.08	4982.73	4966.29	4957.50	4957.48
4938.99	4920.68	4919.19	4891.68	4890.94	4878.41
4872.31	4871.49	4859.94	4789.80	4737.00	4707.51
4691.59	4679.03	4668.36	4667.62	4654.76	4647.60
4638.19	4637.68	4625.25	4619.46	4611.47	4607.85
4603.09	4598.32	4592.82	4556.28	4548.01	4531.31
4528.84	4525.32	4494.74	4484.42	4482.40	4476.25
4469.58	4466.75	4461.83	4459.29	4454.55	4447.90
4443.35	4442.52	4433.37	4430.79	4427.49	4422.74
4415.30	4408.59	4407.85	4404.94	4401.51	4391.14
4388.62	[d] 4383.72	4376.10	4369.94	4367.73	4352.90
4337.20	[f] 4325.94	4315.23	4309.55	[G] 4308.07	4305.63
4299.44	4294.31	4285.62	4282.54	4271.92	4271.35
4268.02	4260.67	4250.96	4250.30	4247.65	4245.40
4239.95	4239.03	4236.14	4233.81	4227.65	4225.66
4224.32	4222.39	4219.52	4217.74	4216.33	4210.53
4204.12	4202.18	4199.26	4198.47	4196.36	4195.51
4191.62	4187.97	4187.22	4185.06	4182.51	4181.91
4177.71	4176.67	4175.76	4175.03	4172.86	4172.25
4171.04	4158.94	4157.95	4156.93	4155.00	4154.62
4154.09	4149.49	4147.79	4144.01	4143.58	4137.11
4134.82	4133.01	4132.20	4127.73	4122.64	4121.97
4118.72	4114.60	4109.93	4107.65	4104.25	4100.88
4098.31	4096.11	4085.43	4085.12	4084.64	4079.96
4078.46	4076.77	4074.92	4071.90	4070.90	4068.12
4067.41	4067.09	4063.75	4062.60	4057.96	4045.97
4034.64	4033.21	4030.89	4022.02	4014.68	4009.85
4005.31	3998.22	3997.54	3986.32	3984.08	3981.91
3977.90	3971.48	3969.39	3956.82	3952.76	3951.30
3950.10	3948.92	3942.58	3941.03	3935.97	3933.80
3930.37	3928.06	3923.05	3920.41	3917.34	3916.88
3906.63	3904.05	3903.11	3899.85	3898.10	3895.80
3888.68	3887.22	3878.71	3886.42	3878.17	3873.93
3872.66	3867.38	3865.70	3860.04	3859.39	3856.52
3852.76	3851.01	3850.16	3847.01	3843.41	3841.24
3840.58	3839.43	3836.53	3834.42	3827.97	3826.02
3824.63	[L] 3820.56	3815.98	3813.17	3806.89	3805.49
3799.70	3798.66	3797.70	3795.15	3790.27	3788.03
3779.63	3767.33	3765.71	3763.94	3758.38	3749.62
3748.41	3746.05	3745.71	3743.51	3738.48	3737.26
3735.49	3735.01	3732.55	[M](3727.77	3727.17)	3724.55
3722.69	3720.05	3716.59	3709.37	3708.07	3704.63
3701.24	3694.17	3687.81	3687.62	3686.14	3682.39

3669.69	3659.64	3651.65	3647.95	3640.57	3631.59
3623.37	3622.19	3621.65	3618.89	3617.98	3610.33
3609.03	3606.87	3605.66	3594.75	3587.14	3586.24
3584.82	[N]3581.34	3574.04	3572.16	3570.23	3565.53
3558.69	3557.03	3555.08	3545.78	3542.24	3541.20
3536.69	3533.34	3527.94	3526.55	3526.29	3521.40
3513.97	3497.99	3497.27	3490.72	3489.78	3476.85
3475.56	3471.44	3465.97	3460.06	3452.39	3452.03
3450.44	3447.41	3445.26	3444.02	[O] 3441.13	3440.70
3428.30	3427.24	3426.75	3426.48	3425.12	3424.40
3422.73	3418.61	3417.96	3415.65	3413.26	3410.30
3407.57	3406.96	3404.44	3402.37	3401.64	3399.43
3394.69	3392.76	3384.07	3380.21	3379.15	3378.78
3370.91	3369.66	3366.92	3355.33	3348.03	3342.39
3340.68	3337.77	3329.04	3323.88	3314.87	3310.57
3307.37	3306.48	3306.10	3298.24	3292.74	3292.17
3291.14	[Q] 3286.87	3280.41	3274.09	3271.11	3265.72
3257.73	3254.51	3251.32	3248.35	3244.31	3239.54
3234.11	3231.07	3227.92	3225.91	3222.16	3219.91
3219.70	3217.53	3216.07	3214.14	3212.12	3205.49
3200.58	3199.66	3197.08	3193.41	3192.89	3191.81
[R] 3180.34	3178.12	3175.54	3171.48	3166.59	3166.01
3162.08	3160.74	3158.03	3157.19	3153.35	3151.42
3144.10	3142.58	3134.25	3132.65	3126.29	3125.76
3119.62	3116.73	3102.80	3100.78	[S ₂]3100.42	3100.06
3098.29	3093.96	3091.71	3083.84	3075.82	3067.35
3059.23	3057.54	3055.39	3053.17	[s] 3047.70	3045.20
3042.79	3042.17	3041.87	3040.58	3037.49	3037.41
3031.78	3031.35	3030.28	3026.61	3025.96	3024.15
[T](3021.19	3020.76)	3019.09	3017.75	3016.29	3011.61
3009.70	3008.23	3007.34	3003.18	3001.04	3000.60
2999.63	[t] 2994.52	2991.82	2990.48	2987.40	2985.69
2984.96	2983.67	2981.99	2981.57	2980.66	2976.23
2973.36	2973.25	2970.22	2969.56	2967.00	2965.38
2960.11	2957.61	2957.48	2957.42	2954.06	2953.90
2953.61	2950.38	2949.32	2948.56	[U]2947.99	2947.81
2944.53	2941.46	2937.94	2937.02	2929.13	2926.69
2925.47	2923.96	2923.43	2920.79	2918.14	2914.37
2912.27	2909.60	2909.00	2907.60	2902.05	2901.48
2899.52	2898.55	2895.14	2894.60	2892.59	2887.91
2886.41	2883.82	2881.68	2880.87	2877.40	2874.27
2872.41	2869.41	2866.71	2863.95	2863.48	2862.59
2858.99	2853.84	2852.22	2851.89	2850.72	2848.80
2846.90	2845.66	2844.08	2843.74	2840.53	2840.09
2838.23	2835.54	2832.53	2828.90	2825.78	2825.67

2824.45	2823.37	2819.38	2817.58	2815.61	2813.39
2808.40	2807.08	2804.59	2803.71	2801.18	2798.36
2797.85	2795.61	2795.03	2794.80	2792.47	2791.87
2791.54	2789.90	2788.20	2788.08	2783.78	2781.95
2779.37	2778.92	2778.32	2778.18	2774.79	2773.31
2772.21	2769.40	2767.62	2767.02	2764.44	2763.20
2762.85	2762.11	2761.88	2760.99	2759.89	2757.94
2757.41	2756.43	2755.83	2754.51	2754.12	2753.77
2753.40	2750.98	2750.24	2749.64	2749.45	2749.26
2747.67	2747.08	2746.57	2745.16	2744.63	2744.16
2743.66	2743.26	2742.48	2739.62	2737.40	2737.05
2735.74	2735.64	2735.54	2734.42	2733.67	2730.82
2728.93	2728.14	2727.64	2726.23	2725.00	2723.67
2720.99	2720.31	2719.54	2719.12	2718.54	2714.51
2711.74	2710.64	2708.67	2706.68	2706.10	2704.09
2699.21	2697.11	2696.44	2696.15	2690.15	2689.95
2689.31	2680.56	2679.16	2673.31	2669.60	2668.00
2667.08	2666.97	2666.46	2664.77	2662.16	2661.32
2660.51	2656.88	2656.24	2651.81	2647.67	2645.55
2644.08	2641.77	2635.90	2631.40	2631.12	2628.39
2625.75	2623.61	2621.75	2620.50	2617.70	2615.53
2613.94	2611.96	2607.19	2605.80	2604.93	2599.49
2598.46	2594.23	2593.78	2591.64	2588.14	2585.95
2584.63	2582.53	2579.95	2578.04	2576.77	2576.23
2575.86	2574.46	2572.85	2570.59	2569.76	2566.99
2563.56	2562.61	2560.68	2556.95	2556.41	2553.35
2551.22	2549.68	2548.79	2547.09	2546.29	2544.86
2544.05	2542.23	2541.06	2539.01	2537.24	2536.93
2535.70	2533.89	2532.40	2530.82	2529.43	2528.60
2527.50	2527.33	2526.33	2525.51	2525.14	2524.35
2523.79	2523.22	2522.92	2522.00	2521.12	2518.19
2517.79	2517.28	2516.22	2514.41	2512.41	2511.08
2510.91	2508.81	2508.02	2507.01	2505.67	2503.53
2502.56	2501.90	2501.20	2498.99	2497.91	2497.18
2496.63	2496.04	2493.30	2491.24	2491.01	2489.07
2488.24	2484.28	2483.34	2480.28	2480.04	2472.85
2476.80	2474.91	2473.18	2472.86	2472.43	2469.00
2467.83	2466.84	2465.23	2462.74	2461.31	2460.40
2458.81	2457.68	2453.56	2447.84	2444.61	2443.97
2442.65	2440.28	2439.85	2439.39	2438.30	2436.48
2435.07	2431.11	2430.19	2429.56	2424.23	2421.82
2413.39	2411.19	2410.60	2406.74	2404.96	2404.51
2399.31	2395.72	2391.56	2388.73	2384.51	2383.27
2382.12	2380.85	2379.41	2375.33	2373.82	2370.59
2368.69	2366.69	2364.91	2362.14	2360.40	2360.09

2359.20	2354.96	2348.39	2344.40	2344.12	2343.56
2338.11	2332.86	2331.41	2327.45	2320.43	2313.20
2309.08	2303.55	2298.25	2297.88	2293.98	2291.21
2289.06	2230.13	2227.81	2214.70		

LANTHANUM.

The spark-spectrum of lanthanum is rich in lines which have been measured by Kirchhoff,¹ and more especially by Thalén.²

Spark-spectrum:

6393.5	6250.0	5974.0	5930.0	5805.5	5795.0	5791.5	5788.0
5770.0	5674.0	5632.0	5588.0	5501.5	5455.5	5381.0	5381.5
5376.5	5340.5	5303.5	5302.8	5302.0	5188.5	5183.5	5176.5
5123.0	4526.5	4525.0	4523.0	4431.0	4428.0	4385.0	4383
4330.5	4322.5	4295.5	4286.5	4268.5	4263.5	4238.5	4235.5
4217.0	4196.5	4192.0	4152.0	4142.5	4122.0	4086.5	4077.0
4042.5	4031.5	3947.0					

LEAD.

The arc-spectrum is obtained by the use of leaden electrodes, preferably in an atmosphere of hydrogen, so as to avoid the production of the oxide bands which were observed by Plücker and Hittorf³ on passing sparks through a Geissler tube containing lead chloride vapor. The arc-spectrum differs materially from that of the spark; it has been investigated by Liveing and Dewar,⁴ and more recently by Kayser and Runge.⁵ Lockyer and Roberts⁶ observed that, at low temperatures, lead vapor produces an absorption-spectrum in the red and blue. All lead compounds exhibit the channelled oxide-spectrum consisting of the bands of $\lambda = 5905$, 5685, 5611, and 5461; they shade off towards the red, and have been described by Mitscherlich,⁷ Plücker and Hittorf, and

¹ A. B. A. 1861.

² Kongl. Svenska Vetensk. Akad. Handl. (1874) 12, No. 4. See also Bunsen, P. A. 155, 366. Clève, C. r. 95, 33.

³ P. T. 155, 25.

⁴ P. R. S. (1879) 29, 402. P. T. (1882) 174, 187.

⁵ A. B. A. 1893.

⁶ P. R. S. 23, 344. Lockyer, P. T. 163, 253, 369.

⁷ P. A. 121, 468.

Lecoq de Boisbaudran.¹ In the Bunsen flame they are too fugitive to be observed with certainty, but H. W. Vogel² has constructed an apparatus which permits of the addition of lead chloride vapor to a hydrogen or coal-gas flame, and renders them much more permanent.

Arc and spark spectra:

6657.4*	6453.3*	6041.2*	6002.08	5875.1*	5608.0*	5547.2*
5373.4*	5201.65	5045.9*	5005.62	4387.3*	4246.6*	4057.97
3740.10	3683.60	3639.71	3572.88	3262.47	3240.31	3220.68
2873.40	2833.17	2823.28	2802.09	2697.72	2663.26	2650.77
2614.26	2577.35	2476.48	2446.28	2443.92	2428.71	2411.80
2402.04	2393.89	2332.54	2247.00	2237.52	2175.88	2170.07
2115.1	2112.0	2088.5				

LITHIUM.

Lithium salts are dissociated in the Bunsen flame and exhibit two lines belonging to the metal: the one, $\lambda = 6708.2$, is very bright and deep red; the other, $\lambda = 6103.8$, is fainter and orange-colored. Other lines are visible in the spark and arc spectra. Kayser and Runge³ measured eighteen, and Liveing and Dewar⁴ observed two additional ones in the ultra-violet.

Arc and spark spectra:

6708.2†	6103.77†	4972.11	4602.37	4132.44	3915.2	3232.77	2741.39
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MAGNESIUM.

The bibliography shows how frequently the magnesium-spectrum has been subjected to exhaustive investigation; it

¹ Spectres lumineux (Paris, 1874).

² Prakt. Spectralanal. (Berlin, 1889). See also Thalén, N. A. S. U. (1868) [3] 6. Kirchhoff, A. B. A. 1861. Huggins, P. T. 154, 139. Hartley and Adeney, P. T. 175, 163.

³ A. B. A. 1890.

⁴ P. R. S. 28, 367, 471; (1880) 30, 93. P. T. (1883) 174, 215. See also Kirchhoff and Bunsen, P. A. 110, 167. Kirchhoff, A. B. A. 1861. Huggins, P. T. 1864, p. 139. Müller, P. A. 118, 641. Ketteler, P. A. 104, 390. Wolf and Diacon, C. r. 55, 334. Rühlmann, P. A. 132, 1. Thalén, N. A. S. U. (1868) [3] 6. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874).

* Visible only in the spark-spectrum. (Thalén.)

† Visible also in the flame-spectrum of lithium salts.

is obtained by burning the metal in air, by passing sparks through a solution of a magnesium salt, or between electrodes of the metal, and by the combustion of the metal in the carbon arc. Liveing and Dewar¹ examined the flame, spark, and carbon arc spectra in atmospheres of various gases; the spectra are identical, although the lines may differ in brightness. They also observed a number of oxide bands of $\lambda = 5006-4934$ and $3865-3720$; these shade off in the violet. A band between $\lambda = 3634$ and 3621 is also visible in the oxyhydrogen flame. They state that when magnesium is burnt in hydrogen the elements combine, and the resulting product exhibits a band-spectrum between $\lambda = 5618$ and 4803 . Kayser and Runge² have made more recent and accurate measurements of the arc-spectrum, using magnesium powder, or wire, and carbon poles; they were unable to detect the bands of the oxide or hydrogen compound, but the former were plainly visible on burning the metal in air. E. Becquerel³ found the infra-red lines $\lambda = 8990, 10,470, 12,000$, and $12,120$ in the arc-spectrum. Magnesium compounds are not dissociated in the Bunsen flame.

Spark and arc spectra:

5528.75	5183.84*	5172.87*	5167.55*	4703.33	4571.33*	4352.18
3838.44	3832.46*	3829.51*	3336.83	3332.28	3330.08	3097.06
3093.14	3091.18	2942.21	2938.67	2852.22*	2802.80	2795.63
2783.08	2781.53	2779.94	2778.36	2776.80		

¹ P. R. S. **28**, 367; **30**, 93; **32**, 189. P. T. (1883) **174**, 208.

² A. B. A. 1891.

³ C. r. **96**, 1218; **97**, 72. See also Kirchhoff, A. B. A. 1861. Thalén, N. A. S. U. (1868) **6**. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Cornu, Spectre normal du soleil (Paris, 1881). Bunsen, P. A. **155**, 366. Fiévez, Bull. de l'Acad. R. de Belgique (1880), [2] **1**, 91. Hartley and Adeney, P. T. (1884) **175**, 95.

* Also visible in the flame-spectrum. (Liveing and Dewar.)

MAGNESIUM HYDRIDE.¹

Bands extending towards the red:

5619 5567 5514 5513 5512 5211 5181 4850 4804

MAGNESIUM OXIDE.¹

Bands extending towards the red:

5001 4991 4981 4970

MANGANESE.

The spark-spectrum of manganese has been measured by Huggins,² and by Thalén;³ the arc-spectrum by Ångström,⁴ and Thalén, and in part by Lockyer,⁵ and Cornu.⁶ The spectra are not identical, and they have not been the subject of recent investigation except by Hartley,⁷ who examined the oxyhydrogen flame-spectrum of manganese, and manganese oxide.

Potassium permanganate exhibits the most characteristic absorption-spectrum of any manganese compound; it has been investigated by Gladstone,⁸ Brewster,⁹ and H. W. Vogel.¹⁰ The last states that the spectra of the solid salt and of the solution are similar, but not identical; the spectrum of potassium manganate is quite different (comp. following chapter). The determination of potassium permanganate by spectro-colorimetric methods is described in G. and H. Krüss' work on Colorimetry and Quantitative Spectrum Analysis.

¹ Liveing and Dewar, P. R. S. 28, 367; 30, 93; 32, 189.

² P. T. (1864) p. 139.

³ N. A. S. U. (1868) [3] 6. Le spectre du fer, 1884.

⁴ Recherches sur le spectre solaire (Upsala, 1868).

⁵ P. T. (1873) 163, 270.

⁶ Spectre normal du soleil (Paris, 1881).

⁷ P. R. S. (1894) 56, 192. P. T. (1894) 185, 1029. See also Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Liveing and Dewar, P. R. S. (1879) 29, 402.

⁸ Jour. Chem. Soc. 10, 79. P. M. [4] 24, 417.

⁹ *Ibid* [4] 24, 441.

¹⁰ Ber. 11, 916. Monatsber. Berl. Akad. 1878. p. 412.

Arc and spark spectra:

6022.0	6016.9	6013.7	5420.6*	5413.5*	5377.7*	5341.3*
4823.7	4783.6	4765.9	4762.3	4754.2	4739.2	4730.0
4727.6	4710.0	4671.6†	4626.4†	4607.4†	4605.6†	4548.9†
4502.3	4499.0	4490.2	4473.1	4470.1	4464.9	4462.1
4461.3	4458.3	4457.5	4456.0	4455.4	(4455.1†)	4454.9†
4451.8	4436.3	4414.9	4382.2†	4375.1†	4337.6†	4325.9†
4284.5†	4281.3	4272.2†	4266.3	(4260.9	4258)	4235.4
4227.6	4083.8	4080.3	4055.0	4048.9	4041.3	4033.2
4030.9						

MANGANESE OXIDE.¹

Spark-spectrum:

6235	6205 b	6186	6179 b	5933	5848 b	5689	5684	5645 b	5608 b
5560	5434	5424 b	5396	5392 b	5360 b	5230 b	5193 b	5158 b	

MERCURY.

The earlier observers measured the spark-spectrum under the ordinary pressure, or under reduced pressure in a Geissler tube. Liveing and Dewar² were unable to obtain the arc-spectrum, but Kayser and Runge³ succeeded in doing so without difficulty.

Arc and spark spectra:

6152.6†	5889.1*	5790.49	5769.45	5460.97	4916.41	4358.56
4347.65	4078.05	4046.78	3663.25	3654.94	3650.31	3390.50
3341.70	3131.94	3131.68	3125.78	2957.37	2925.51	2893.67
2759.83	2752.91	2655.29	2653.89	2652.20	2642.70	2576.31
2536.72	2534.89	2464.15	2446.96			

¹ Lecoq de Boisbaudran, *Spectres lumineux* (Paris, 1874). Watts, P. M. [4] **45**, 81. Hartley, P. T. (1894) **185**, 1029.

² P. T. (1883) **174**, 218.

³ A. B. A. 1891. See also Kirchhoff, A. B. A. 1861. Huggins, P. T. (1864) p. 139. Gladstone, P. M. [4] **20**, 249. Plücker, P. A. **107**, 497. Thalén, N. A. S. U. (1868) [3] **6**. Lecoq de Boisbaudran, *Spectres lumineux* (Paris, 1874). Hartley and Adeney, P. T. **175**, 136. Pearce, W. A. **6**, 597. H. W. Vogel, *Berl. Monatsber.* 1879, p. 586. Eder and Valenta, *Denkschr. Wiener Akad.* (1894) **61**, 401.

* Visible only in the spark-spectrum. (Thalén.)

† Visible only in the arc-spectrum. (Thalén.)

MOLYBDENUM.

The spectrum of this element has not been thoroughly investigated. Thalén,¹ using Leyden jars, examined the visible portion of the spark-spectrum; Lockyer,² in addition, observed about 35 arc lines between $\lambda = 4000$ and 3900; and W. A. Miller³ photographed some lines in the ultra-violet, but did not measure them.

Spark-spectrum:

6030.2	5888.6	5857.6	5792.0	5751.2	5688.6	5570.2	5532.6
5506.1	4278.3						

NICKEL.

Thalén⁴ used nickel electrodes in order to obtain the spark-spectrum, and Lecoq de Boisbaudran⁵ passed sparks through nickel chloride solutions; like Kirchhoff,⁶ they only examined the visible portion. Ångström's⁷ investigations of the arc-spectrum were limited to the same region. Cornu,⁸ Lockyer,⁹ and, more recently, Liveing and Dewar,¹⁰ have examined portions of the spectrum, particularly the ultra-violet; and Hasselberg¹¹ has recently completed a careful investigation of the spectrum between D and $\lambda = 3450$. The absorption-spectra¹² of solutions of nickel salts are not very

¹ N. A. S. U. (1868) [3] 6.

² P. T. 173, 561. P. R. S. 27, 280.

³ P. T. (1862) 152, 861.

⁴ N. A. S. U. (1868) [3] 6.

⁵ Spectres lumineux (Paris, 1874).

⁶ A. B. A. 1861.

⁷ Recherches sur le spectre solaire (Upsala, 1868).

⁸ Spectre normal du soleil (Paris, 1881).

⁹ P. T. 163, 369; 173, 561.

¹⁰ *Ibid.* (1888) 179, 231.

¹¹ Svensk. Vetensk. Akad. Handl. (1896) 28, No. 6. Astrophys. Jour. (1896) 3, 288; 4, 343; (1897) 5, 38.

¹² H. W. Vogel, Ber. (1875) 8, 1537.

characteristic; the majority produce total extinction at each end.

Arc and spark spectra:

6177.0	5893.13	5761.10	5754.86	5715.31	5712.10	5709.80
5695.22	5682.44	5664.28	5649.90	5625.56	5615.00	5594.00
5592.44	5588.12	5578.98	5510.28	5477.13	5436.10	5371.64
5168.83	5155.92	5146.64*	5142.96	5137.23*	5129.52	5115.55*
5100.13	5099.50	5084.27	5082.55	5081.30	5080.70	5049.01
5042.35	5035.55	5017.75	5000.48	4984.30	4980.36	4918.53
4904.56	4866.42	4855.57	4831.30	4829.18	4786.66	4756.70
4714.59	4703.96	4686.39	4648.82	4606.37	4605.15*	4600.51
4592.69	4547.44	4520.20	4470.61	4462.59*	4459.21	4437.17
4410.70	4401.70	4384.68	4359.73	4331.78	4330.85	4325.75
4296.06	4288.16	4284.83	4201.88	4195.71	4128.48	3995.45
3973.70*	3972.31	3944.25	3889.80	3863.21	3858.40	3832.44
3831.82	3829.49	3807.30*	3793.75	3792.48	3783.67*	3775.71
3772.70	3744.68	3739.36	3736.94	3722.63	3688.58	3674.28
3670.57	3664.24	3624.87	3619.52	3612.86	3610.60*	3609.44
3602.41	3597.84	3588.08	3571.99	3566.50	3551.66	3548.34
3528.13	3524.65	3919.90	3515.17	3514.06	3510.47*	3501.00
3493.10	3486.04	3472.68	3469.64	3467.63	3461.78	3458.59
3453.0	3446.4	3437.8	3434.1	3424.2	3415.5	3415.1
3414.6	3408.3	3394.1	3392.1	3381.7	3375.0	3370.6
3362.6	3321.9	3317.3	3244.5	3236.0	3234.4	3197.4
3179.6	3134.0	3101.99	3101.67	3087.0*	3080.7	3064.6
3057.6*	3054.3	3050.8	3037.9	3019.2*	3011.9	3003.6
3002.5	2994.5	2992.6	2981.6	2943.9	2936.7*	2928.8*
2913.6	2865.5†	2863.7*	2821.2	2805.4	2684.4*	2679.2*
2647.2	2639.9*	2615.3*	2610.0*	2545.8	2511.0	2506.3*
2484.0	2473.2	2454.1	2441.9	2437.9	2421.2	2416.4
2413.2	2394.7	2394.4	2393.0	2382.2	2375.4	2356.3
2345.1	2341.1*	2334.5	2330.0	2326.4	2325.9	2321.4
2319.7	2318.4*	2316.0	2314.0	2312.2	2311.0	2303.7
2302.9*	2302.4*	2296.6*	2287.8	2287.2	2278.8	2278.2
2274.5	2270.3	2264.5	2258.0	2256.1	2255.1	2253.9
2244.8	2230.0	2226.2	2224.7	2222.7	2220.2	2216.2
2210.2	2206.5	2205.6	2201.2	2184.6	2174.8	2174.2

NIOBIUM.

Thalén unsuccessfully endeavored to measure the lines, which are very faint.

* Visible only in the spark-spectrum. † Visible only in the arc-spectrum.

NITROGEN.

In addition to the ordinary spark or elementary spectrum, two band-spectra are known, one produced at the cathode, the other at the anode, when a feeble discharge is passed through the gas contained in a Geissler tube. The spectrum obtained with powerful sparks consists of numerous lines which are bright, but not quite sharp; they have been measured by Huggins and Thalén,¹ whilst Hartley and Adeney² subsequently examined the blue and violet ones. Plücker first observed the band-spectrum at the anode in 1858; it was noticed a little later by van der Willigen;³ Plücker and Hittorf,⁴ and Lecoq de Boisbaudran, published drawings of it; and it was accurately measured by Ångström and Thalén,⁵ and more recently by Hasselberg.⁶ Ångström and Thalén believed that the spectrum was not due to nitrogen, but to an oxygen compound, and this view was supported by Schuster,⁷ who observed that the spectrum disappears if the gas is heated with sodium, which he thought absorbed the oxygen; but Salet⁸ showed that the spectrum is obtained in these circumstances if the metal is previously saturated with nitrogen. Since that time this spectrum has been universally ascribed to nitrogen; it consists of channelled spaces sharply defined towards the red, and shading off towards the violet. Hasselberg and Piazzzi-Smyth,⁹ using instruments of high dispersive

¹ N. A. S. U. (1875) [3] 9. (From 5942.7 to 4641.0.)

² P. T. (1884) 175, 91. (From 4629.7 to 3995.2.)

³ P. A. 106, 610.

⁴ P. T. 155, 1.

⁵ N. A. S. U. (1875) [3] 9.

⁶ Mém. de l'Acad. St. Pétersb. (1885) [7] 32, No. 15.

⁷ P. R. S. 20, 482.

⁸ A. c. p. [4] 28, 52. C. r. 82, 223, 274.

⁹ P. T. E. 32, 416. See also Ångström, P. A. 94, 141. Willner, P. A. 135, 524; 137, 356; 147, 325; 149, 103. H. C. Vogel, P. A. 146, 569. Deslandres, C. r. 103, 375. A. c. p. [6] 14, 257.

power, succeeded in resolving the bands into groups of separate lines. The band-spectrum at the cathode was differentiated from that at the anode in 1858 by Dove,¹ and van der Willigen,² but subsequently Plücker and Hittorf stated that they were identical. The principal bands were measured ten years later by Ångström and Thalén.³ Hasselberg⁴ subsequently resolved them into bright sharp lines, which are totally different from those at the cathode, although their appearance is similar. Trowbridge and Richards⁵ state that, with a powerful continuous discharge, nitrogen exhibits its channelled spectrum, but the introduction of a condenser causes a change to the bright line-spectrum. In connection with nitrogen the spectra of some of its compounds and of air are of interest. The line-spectrum of *air* is composed of the spectra of nitrogen and oxygen; it is always observed when sparks are passed between metal electrodes in air, and requires particular notice in order to avoid errors in the investigation of spark-spectra. The air lines usually extend equally sharply over the whole breadth of the spectrum, whilst the metallic lines often form aggregates proceeding from the poles. An absorption-spectrum is produced by considerable thicknesses of air, particularly in presence of water vapor; in solar observations this causes some of the Fraunhofer lines, the intensity of which differs with the position of the sun, and depends on the thickness of air which its rays traverse.

Ammonia exhibits a line-spectrum when burnt in air in a hydrogen flame, or in oxygen in an oxyhydrogen flame; it has been measured by Dibbits, Hofmann, Lecoq de Boisbaudran, Magnanini, and Eder. The principal band extends from the

¹ P. A. 104, 184.

² *Ibid.* 106, 626.

³ N. A. S. U. (1875) [3] 9.

⁴ Mém. de l'Acad. de St. Pétersb. (1885) [7] 32, No. 15. See also H. C. Vogel, P. A. (1872) 146, 569. Déslandres, C. r. 103, 375. A. c. p. (1888) [6] 14, 257.

⁵ Amer. Jour. Sci. (1897) [4] 3, 117. P. M. 43, 135.

red to the beginning of the violet, and consists of numerous lines or bands, some sharp and some aggregated, but showing no regularity in structure. A second band is composed of sharp lines; the remaining five bands closely resemble each other in structure. Their sharp edges are directed towards the red, and the other ends may be resolved into numerous slender lines grouped with tolerable regularity.

Amines when burnt in oxygen do not exhibit characteristic spectra.

Nitrous Anhydride ($\text{NO} + \text{NO}_2$) gives an absorption-spectrum which was observed by Brewster in 1832, but not described until 1860; his drawing cannot be reduced to measurements, as no scale is given. The spectrum was accurately examined by Hasselberg in 1878 between B and $\lambda = 4600$; it is extremely complex, partly because it varies with the quantity of gas, partly from the large number of lines and bands, which are not arranged according to any definite plan.

The spectra of the electric discharge in liquid nitrogen, air, and oxygen have been investigated by Liveing and Dewar;¹ they consist of a continuous spectrum, of bright lines derived from the electrodes, and of comparatively feeble bands apparently emanating from the molecules of the liquid. The continuous spectrum is also probably due to the electrodes. Brühl² has determined the spectrometric constants of nitrogen, and has endeavored to elucidate the spectro-chemical relationship of its compounds.

Line-spectrum of nitrogen:

5942.7	5933.1	5679.1	5675.6	5667.1	5542.2	5535.1
5531.1	5496.1	5480.0	5045.9	5025.9	5016.9	5010.9
5005.9	5002.9	4994.4	4988.0	4804.1	4789.1	4780.1
4641.0	4629.7	4606.4	4600.9	4446.8	4348.8	(4237.0
4229.5)	3995.2					

¹ P. M. [5] 38, 235. Ber. (1895) 28, 4.

² Ztschr. phys. Chem. 16, 193, 225. Ber. 26, 806, 2508; 28, 2388, 2393, 2399.

Band-spectrum at the anode. Lines at the commencement of the bands:

6623.4	6544.4	6468.3	6394.2	6322.4	6252.6	6185.5
6126.9	6069.4	6013.4	5958.9	5905.6	5854.1	5803.9
5754.8	5707.3	5660.2	5614.9	5570.1	5515.4	5478.4
5442.1	5407.2	5372.6	5339.5	5306.7	5275.0	5244.1
5213.7	5184.5	5155.4	5126.9	5099.5	5069.1*	4976.6
4918.6*	4723.6*	4649.4*	4574.3*	4490.2*	4416.6*	4357.5
4270.0*	4201.6*	4141.7*	4094.9	4059.3*	3998.5*	

Band-spectrum at the cathode. Lines at the commencement of the bands:

5228.5	4709.5	4652.1	4600.2	4554.6	4516.1	4485.7
4278.6	4236.9	4199.3	4167.0			

AIR.

Spark-spectrum:¹

6563.1	5942.6	5933 1	5679.1	5775.6	5667.1	5542.2	5535.1
5531.1	5496.1	5480.0	5045.9	5025.9	5016.9	5011.0	5006.0
5003.0	4994.5	4988.0	4804.1	4789.1	4780.1	4707.6	4699.1
4648.0	4642.0	4629.7	4606.4	4600.9	4446.7	4416.2	4414.3
4348.8	4319.3	4241.2	4237.0	4229.5	4075.8	4072.1	4069.9
3995.2	3973.2	3955.5	3919.2	3749.6	3727.1	3438.1	3333.7
3331.5	3309.2						

Absorption-spectrum.² Telluric Fraunhofer lines. See also Rowland's table of wave-lengths, p. 191:

¹ Thalén, N. A. S. U. (1868) [3] **6** (w.-l. 6563.1-4699.1). Hartley and Adeney, P. T. (1884) **175**, 91 (w.-l. 4648.0-3309.2). Kirchhoff, A. B. A. 1861. Huggins, P. T. (1864) **154**, 139. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Plücker and Hittorf, P. T. (1865) **155**, 1. Goldstein, W. A. (1882) **15**, 280.

² Becker, T. R. S. E. (1890) **36**, 1. Brewster, P. T. E. 1833. Brewster and Gladstone, P. T. (1860) **150**. Ångström, Recherches sur le spectre solaire (Upsala, 1868). Piazzzi-Smyth, Madeira spectroscopic (Edinb. 1882). Fiévez, Spectre solaire (Bruxelles, 1883). Egoroff, C. r. **97**, 555; **101**, 1143. Hautefeuille and Chappuis, C. r. **93**, 80. Cornu, A. c. p. [6] **7**, 1. C. r. **95**, 801. Abney, P. R. S. (1885) **348**. C. r. **97**, 1206. Hennesay, P. R. S. (1870) **19**. P. T. (1875) **165**. Langley, C. r. **97**, 555. Janssen, A. c. p. (1871) [4] **23**; C. r. (1863) **56**, 538; (1865) **60**, 213; (1866) **63**, 289; (1874) **78**, 995; (1885) **101**, 111, 149; (1886) **102**; (1888) **106**; (1888) **107**; (1889) **108**. Secchi, C. r. (1865) **60**, 379. Thollon, Ann. de l'Obs. de Nice (1890) **3**.

* Triplets.

6020.33	5999.83	5997.43	5994.74	(5992.17	5992.01)	5991.03
5990.74	5989.44	(5988.75	5988.67)	5987.20	5985.37	5977.94
5977.14	5976.94	5975.27	5971.53	5970.24	5969.24	5968.49
5967.87	5967.66	5966.81	(5966.42	5966.33)	5962.65	5958.85
(5958.48	5958.42)	5958.02	5955.10	5951.68	5950.49	5949.92
5949.42	5949.25	5948.35	5947.24	5947.02	5946.14	5945.81
5945.39	5944.84	5944.42	5942.73	5942.57	5941.73	5941.19
5935.96	5932.96	5932.28	(5928.53	5928.43)	5925.19	5924.49
5923.98	5923.82	5922.66	5920.73	5919.85	5919.22	5918.62
5913.15	(5910.95	5910.87)	5910.25	5909.14	5902.25	5901.68
5900.22	5900.06	5899.17	5898.39	5896.97	5895.26	5895.11
5893.72	5892.59	5891.87	5891.73	5890.34	5889.78	5887.36
5886.12	5884.04	5859.73	5745.92	5742.30	5737.82	5727.18
5722.07	5719.75	5699.52	5698.31	5692.57	5690.62	5687.66
5125.20	5068.88	5067.29	5060.19	5056.58	5018.55	

AMMONIA.¹

Flame-spectrum:

Band α	6667—3572:	6330	6293	6189	6051	6006	5973	5950
		5703	5694	(5271	5263)			
Band β	3433—3396:	3370.8	3360.3					
Band γ	2719— ? :	2719.2	2718.1	2710.9	2709.1			
Band δ	2595—2500:	2595.6	2594.3	2587.7	2586.2			
Band ϵ	2479—2406:	2478.8	2477.4	2471.5	2470.3			
Band ζ	2371—2308:	2370.8	2370	2364.5	2363.4			
Band η	2272—2210:	2272	2271	2265	2263			

NITROUS ANHYDRIDE.² ($\text{NO}_2 + \text{NO}$.)

Absorption-spectrum:

6165.7	6127.3	6122.1	5929.1	5921.4	5790.7	5753.5	5730.4
5654.0	5645.6	5643.1	5636.7	5634.0	5531.5	5529.2	5490.7
5463.3	5452.1	5431.3	5393.5	5390.4	5385.3	5380.2	5340.2
5264.6	5260.2	5252.3	5243.8	5241.2	5230.6	5225.1	5220.0

¹ Magnanini, Atti della R. Accad. dei lincei [4], 5, 900 (w.-l. 6667-4493). Eder, Denkschr. Wiener Akad. (1893) 60 (w.-l. 5080-2210). Dibbitts, Die spectraal Analyse, 1863. P. A. (1864) 122, 497. Schuster, B. A. R. 1872. Mitscherlich, P. A. (1863) 121, 459. Lecoq de Boisbaudran, C. r. 101, 43. Hofmann, P. A. (1872) 147, 92.

² Hasselberg, Mém. de l'Acad. St. Pétersb. (1878) [7] 26, No. 4. Brewster, P. T. E. 12, 519. P. A. 28, 385; 37, 50. P. T. (1860) 150, 157. Morren, P. A. 141, 157. Gernez, C. r. 74, 465. Moser, P. A. 160, 177. Bell, Am. Chem. J. (1885) 7, 32.

5215.8	5208.0	5200.7	5196.0	5191.8	5124.8	5096.0	5046.5
5032.8	5028.0	4966.6	4964.8	4947.2	4942.7	4903.9	4886.4
4883.2	4813.0	4798.2	4793.8	4747.6	4680.6	4644.6	

OSMIUM.

Thalén¹ observed only a single line in the spectrum of this element; Huggins,² in the visible region, noticed seventeen others, and Lockyer³ four additional ones between $\lambda = 4000$ and 3900 . Rowland and Tatnall⁴ have recently measured the arc-spectrum between $\lambda = 3000$ and 4600 ; the lines are all comparatively faint, especially the double one.

Arc and spark spectra:

4422.7*	4420.633	4260.993	4135.945	(4097.090	4097.004)	4066.848
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OXYGEN.

The spark-spectrum of air was first measured by Ångström⁵ (comp. nitrogen), who did not distinguish the oxygen from the nitrogen lines; this was first done by Huggins.⁶ Plücker and Hittorf⁷ examined the spectrum of oxygen enclosed in a Geissler tube, but failed to get concordant results in consequence of the presence of carbon monoxide, which is so readily produced. Schuster⁸ found a compound line-spectrum at the anode, and a band-spectrum at the cathode. The elementary line-spectrum is obtained by passing sparks from a Leyden jar through oxygen under the ordinary pressure.

The absorption-spectrum is only produced by a considerable thickness of the gas; it is the origin of some of the

¹ N. A. S. U. (1868) [3] 6.

² P. T. 1864, p. 139.

³ *Ibid.* (1881) 173, 561. See also Fraser, C. N. 8, 34.

⁴ Astrophys. Jour. (1895) 2, 186.

⁵ P. A. (1855) 94, 141.

⁶ P. T. 154, 146.

⁷ *Ibid.* 155, 23. Plücker, P. A. (1859) 107, 518.

⁸ P. T. (1879) 170, 37. W. A. 7, 670.

* Spark-spectrum.

telluric lines in the solar spectrum. The presence of oxygen in the sun is still an open question. The spectrum of the electric discharge in liquid oxygen consists, according to Liveing and Dewar,¹ of a few obscure absorption-bands. Bright lines produced by the electrodes are also visible, together with a continuous spectrum which is ascribed to solid particles detached from them.

Elementary line-spectrum:

6171.7 (A. & Th.)	5206.4	4816.6	4802.4	4782.6	4710.2	4705.4
4694.1	4651.0	4649.2	4643.4	4641.9	4638.9	4630.7
4614.0	4607.2	4601.4	4596.2	4592.9	4592.0	4590.9
4544.5	4520.5	4507.7	4503.0	4447.1	4417.2	4415.0
4353.7	4351.4	4349.3	4347.9	4345.5	4319.5	4317.2
4190.0	4185.3	4119.4	4109.8	4105.2	4105.0	4076.2
4070.2	3995.1	3981.4	3973.6	3956.2	3954.8	3919.3
3755.3	3749.8 (Tr. & H.)	3139.4	3135.3 (Desl.)			3882.4

Compound line-spectrum. At the anode:

6157.9	5436.5	5330.4	4368.2 (Sch.)
3956.0	3948.9	3824.4	3692.4 2883.5 (Desl.)

Band-spectrum. At the cathode:

b (6010 5960)	b (5900 5840)	b (5630 5553)	b (5292 5205) (Sch.)
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PALLADIUM.

The spark-spectrum of palladium is obtained by means of powerful discharges from a Leyden jar, passed between electrodes of the metal, or through a solution of the chloride.

¹ P. M. 38, 235. Ber. (1895) 28, 4. The spectra of oxygen have also been observed by the following: Trowbridge and Hutchins, P. M. (1887) [5] 24, 302. Deslandres, A. c. p. (1888) [6] 14, 257. Wüllner, P. A. 130, 515; 137, 350; 144, 481; 147, 329. W. A. 8, 253. Salet, A. c. p. [4] 28, 52. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Ångström and Thalén, N. A. S. U. (1875) [3] 9. Paalzow and H. W. Vogel, W. A. 13, 336. Piazz Smyth, P. T. E. (1882) 30, 419. P. M. [5] 13, 130. Janssen, C. r. 118, 1007. Hartley and Adeney, P. T. (1884) 175, 91. Neovius, Bihang til Svenska Det. Akad. Handl. 17, Afd. 1, No. 8. W. A. Beibl. (1893) 17, 563. Eisig, W. A. (1894) 51, 747. Hasselberg, W. A. (1894) 52, 758. Trowbridge, P. M. (1896) 41, 450. Runge and Paschen, Astrophys. Jour. (1896) 4, 317. Lewis E. Jewell, Ibid. (1897) 5, 99.

Some lines in the ultra-violet have been photographed by Hartley,¹ and Rowland and Tatnall² have measured the arc-spectrum between $\lambda = 3000$ –4200. The lines are all comparatively faint.

Arc and spark spectra:

5695.1	5669.1	5641.1	5619.1	5547.2	5543.2
5395.1	5296.1	5234.7	5164.1	5117.4	5110.9
4875.5	4818.1	4788.1	4474.4	4213.1	3958.772*
3894.334*	3690.483*	3634.841*	3609.696*	3571.302*	3553.236*
3517.096*	3489.915*	3481.300*	3460.884*	3441.539*	3433.578*
3421.367*	3404.725*	3337.139*	3302.256*	3258.900*	3251.760*
3242.828*	3114.152*				

PHOSPHORUS.

The line-spectrum is obtained by passing sparks through a Geissler tube containing phosphorus vapor, the band-spectrum by the introduction of phosphorus vapor into a hydrogen flame. The bands are most clearly visible if the flame is cooled by allowing it to impinge on a metal plate against the other side of which a stream of water flows.

Line-spectrum:³

6506	6058	6033	5421	5403	5382	5338	5307
5285	5244	4601	4589 (Pl. & H.)				

Band-spectrum:⁴

5995 b ^r	5606 b	5264 b ^r	5107 b (L. d. B.)
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The bands marked *b^r* are sharply defined towards the red and shade off towards the violet.

¹ P. T. Dublin (1882) [2] 1.

² Astrophys. Jour. (1896) 3, 291. See also Thalén, N. A. S. U. (1868) [3] 6. Kirchhoff, A. B. A. 1861. Huggins, P. T. 1864, p. 139. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Lockyer, P. T. (1881) 173, 561.

³ Plücker and Hittorf, P. T. (1865) 155, 24.

⁴ Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). See also Seguin, C. r. (1861) 53, 1272. Salet, A. c. p. (1873) [4] 28, 56. Christoffe and Beilstein, C. r. (1863) 56, 399. Mulder, J. pr. Chem. (1864) 91, 111. Lockyer, P. R. S. (1874) 22, 374. Hofmann, P. A. 147, 92.

* Arc spectrum.

PLATINUM.

The spark-spectrum is obtained by the use of powerful Leyden jars in conjunction with platinum electrodes, or a solution of platinum chloride. Gouy¹ obtained the spectrum by mixing platinous chloride with the gas in a Bunsen burner. The measurements of Thalén,² Kirchhoff,³ Huggins,⁴ and Lecoq de Boisbaudran⁵ are confined to the visible region. Lockyer⁶ observed twelve lines in the arc-spectrum between $\lambda = 4000-3900$. Rowland and Tatnall⁷ have recently measured the arc-spectrum between $\lambda = 3000-4600$; the lines are all comparatively faint, especially the double one.

The absorption-spectrum of platinum chloride solution consists in a complete extinction of the blue end of the spectrum; solution of potassium platino-chloride exhibits, in addition, a rather large band, the middle of which is situated at $486\mu\mu$.

Arc and spark spectra:

6523.3	5964.7	5479.0	5476.5	5390.6	5368.6	5302.5
5227.2	5060.4	4932.4	4899.0	4879.9	4852.9	4580.8
4560.3	4552.8	4481.8	4455.0	4448.0	4445.7	4442.723*
4440.7	4435.2	4430.4	4392.0	4291.1	(3283.436*	3283.332*)
3064.824*	2998.079*					

POTASSIUM.

The compounds of this element are readily dissociated by the Bunsen flame and exhibit the lines of the metal; the more prominent ones, with a low dispersion, are the pair

¹ C. r. (1877) **85**, 439.

² N. A. S. U. (1868) [3] **6**.

³ A. B. A. 1861.

⁴ P. T. 1864, p. 139.

⁵ Spectres lumineux (Paris, 1874).

⁶ P. T. (1881) **173**, 561. See also Hutchins and Holden, P. M. (1887) [5] **24**, 325. Ciamician, Wien. Ber. [2] **76**, 499.

⁷ Astrophys. Jour. (1895) **2**, 185.

* Arc-spectrum.

$\lambda = 7699$ and $\lambda = 7665$, and the violet one, $\lambda = 4044$. Lockyer¹ believed that four of the potassium lines are visible in the solar spectrum, the absence of the others being due to the dissociation of potassium at the temperature of the sun, and that the visible lines constituted the spectra of the substances into which potassium was resolved. Kayser and Runge's² accurate measurements have shown that potassium lines are absent from the solar spectrum, so that Lockyer's hypothesis is baseless. E. Becquerel³ described the lines $\lambda = 10980$, 11020 , and 12330 in the infra-red.

Arc and spark spectra:

(7699.3	7665.6)*	6938.8	6911.2	5832.23*	5812.54
5802.01*	5782.67*	4047.36	4044.29*	3447.49	3446.49
3217.76	3217.27	3102.37*	3102.15	3034.94	

RHODIUM.

Thalén unsuccessfully endeavored to measure the faint lines in the spectrum of this element, but Rowland and Tatnall⁴ have recently photographed the violet and ultra-violet lines of the arc-spectrum between $\lambda = 3000$ and 4500 .

Arc-spectrum:

4374.981	4211.304	3959.009	3856.654	3701.056	3692.502	3658.135
3597.294	3583.252	3528.177	3502.674	3462.184	3435.039	3396.960

¹ P. R. S. (1878) **27**, 279.

² A. B. A. 1890.

³ C. r. **96**, 1218; **97** 72. See also Bunsen and Kirchhoff, P. A. **110**, 167. Kirchhoff, A. B. A. 1861. Huggins, P. T. 1864, p. 139. Rutherford, Silliman's Journ. [2] **35**, 407. Wolf and Diacon, C. r. **55**, 334. Thalén, N. A. S. U. (1868) [3] **6**. Salet, A. c. p. (1873) [4] **28**, 56. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Liveing and Dewar, P. R. S. **28**, 367, 471; **29**, 398. P. T. (1883) **174**, 215. De Gramont, C. r. (1896) **122**, 1411, 1443.

⁴ Astrophys. Jour. (1896) **3**, 286.

* Visible also in the flame-spectrum.

RUBIDIUM.

This element was discovered in 1860 by Bunsen and Kirchhoff¹ with the help of the spectroscope. The salts are readily dissociated in the Bunsen flame, and the chief lines of the metal are clearly visible; the more prominent are the two violet lines $\lambda = 4215$ and 4202 , and the two red ones, $\lambda = 7811$ and 6298 .

Arc and spark spectra:

7950*	7811*	6298.7*	6206.7*	5724.41*	5648.18*	4215.72*
4201.98*	3591.74	3587.23	3351.03	3348.86		

RUTHENIUM.

The arc-spectrum of this element has been measured by Rowland and Tatnall² between the wave-lengths 2975–4200, the lines are all comparatively faint, especially the double ones.

Arc-spectrum:

4200.062	4080.757	3799.489	3799.042	3728.173	3727.073†	3499.095
3436.883	3428.460	(3264.790)	3264.688)	(3254.834	3254.670)	

SAMARIUM.

This element was termed by its discoverer, Marignac, $Y\beta$. The name samarium was given by Lecoq de Boisbaudran,³ who subsequently, in common with Krüss and Nilson, considered that it was a mixture (comp. didymium).

¹ P. A. 113, 337. See also Kayser and Runge, A. B. A. 1890. Thalén, N. A. S. U. (1868) [3] 6. Kirchhoff, A. B. A. 1861. Lecoq de Boisbaudran, Spectres lumineux (Paris. 1874). Bunsen, P. A. 155, 230, 366. Liveing and Dewar, P. R. S. 28, 367, 471.

² Astrophys. Jour. (1896) 3, 288.

³ C. r. 89, 212, 516; 114, 578; 116, 611, 674. See also Thalén, Öfversigt K. Vetensk. Akad. Förhandl. (1881) 40, No. 7. Soret, C. r. 91, 378. Clève Öfversigt K. Vetensk. Akad. Förhandl. (1881) 40, No. 7.

* Visible also in the flame-spectrum.

† Also Fe.

Spark-spectrum:

5552.1	5516.0	5494.5	5466.5	5452.9	5368.5	5341.4	5320.9	5283.0
5272.0	5252.0	5201.0	5175.4	5173.4	5117.8	5053.3	5044.8	4911.4
4884.4	4848.0	4842.0	4816.0	4786.0	4783.5	4760.5	4746.0	4728.9,
4704.4	4674.4	4669.4	4649.3	4593.8	4581.8	4567.8	4544.8	4538.3
4524.8	4523.3	4520.3	4511.9	4498.8	4478.3	4467.2	4458.2	4454.7
4453.2	4434.2	4425.2	4421.2	4390.7	4347.6	4319.1	4297.1	4280.6
4257.1								

SAMARIUM NITRATE.

Absorption-spectrum.¹ Position of the minimum of brightness:

5797	5759	5588	5282	5211	5005	4892	(4838	4750)	4634	4530
4436	4175	4090								

SCANDIUM.

The discovery of this element was made by Nilson. Thalén² measured its spark-spectrum, which consists of numerous lines; solutions of its salts do not produce absorption-spectra.

Spark-spectrum:

6305.0	6247.0	6239.0	6210.9	6154.1*	6115.9*	6101.5*	6080.1*
6072.6*	6065.1*	6038.0*	5700.5	5687.0	5672.0	5657.5	5641.0
5527.0	5520.5	5514.5	5484.9	5481.9	5392.3	5356.0	5349.4
5240.0	5081.8	5031.3	4744.0	4740.4	4670.4	4415.7	4400.7
4374.6	4325.1	4320.6	4314.6	4249.1			

SELENIUM.

The line-spectrum is obtained by passing sparks from a Leyden jar through a Geissler tube containing selenium vapor; with a feebler current a band-spectrum is produced. Salet³ states that the former is also obtained by passing sparks between platinum electrodes which have been covered with

¹ G. Krüss and Nilson, Ber. 20, 2144.

² Öfversigt K. Vetensk. Akad. Förhandl. (1881) 38, No. 6, p. 13. Journ. de Phys. [2] 35, 446.

³ Spectroscopie (Paris, 1888). A. c. p. (1873) [4] 28, 47.

* Bands shading off towards the red.

melted selenium, whilst he observed the latter in a coal-gas or hydrogen flame in which selenium was burning. Gernez¹ has examined the absorption spectra of the vapors of selenium, selenious chloride, selenious bromide, and selenious anhydride.

Spark-spectrum of the vapor:

6055	5306	5272	5254	5226	5174	5142	5097	5093	4996
4979	(4845	4841)	4764	4648	4604				

Band-spectrum:

5871	5751	5621	5491	5371	5271	5166	5031	4951	4851
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SILICON.

The earlier observers of the visible portion of the spark-spectrum of this element are Plücker,² Kirchhoff, and Salet.³ In Rowland's⁴ table of wave-lengths some lines in the arc-spectrum are given which are not mentioned by previous workers. Concordant measurements in the ultra-violet have been made by Hartley and Adeney,⁵ and Eder and Valenta⁶ of the spark-spectrum, and by Liveing and Dewar,⁷ and Rowland of the arc-spectrum.

Spark-spectrum:

6366	6341	5981	5960	5948.76	5772.36
5708.62	5645.84	5057	5041	(4131.5	4126.5)
4103.10	3905.67	2987.77	2881.70	2631.39	2528.60
2524.21	2519.30	2516.21	2514.42	2506.99	2435.25
2216.76					

¹ C. r. (1872) **74**, 803, 1190. See also Mulder, J. pr. Chem. (1864) **91**, 113. Plücker and Hittorf, P. T. (1865) **155**, 5. C. r. **73**, 622. A. de Gramont, C. r. (1895) **120**, 778.

² P. A. (1859) **107**, 531.

³ Spectroscopie (Paris, 1888). A. c. p. (1873) [4] **28**, 65.

⁴ Astronomy and Astrophysics (1893) **12**, 321.

⁵ P. R. S. **35**, 301.

⁶ Denkschr. d. Wien. Akad. (1893) **60**, 257.

⁷ P. T. **174**, 222. See also Troost and Hautefeuille, C. r. (1871) **73**, 920. Mitscherlich, P. A. (1863) **121**, 459. Ciamician, Wien. Ber. (1880) **82**, 435.

SILVER.

The spark-spectrum of silver has been measured, in the visible portion, by Kirchhoff,¹ Thalén,² Huggins,³ and Lecoq de Boisbaudran,⁴ and a part of the ultra-violet by Hartley and Adeney. Lockyer,⁵ and Liveing and Dewar⁶ only observed a few lines in the arc-spectrum, which was accurately measured by Kayser and Runge.⁷ They obtained the spectrum by volatilizing silver, or crystals of silver nitrate, in the carbon arc. Silver electrodes could not be used, as they at once melted, probably on account of their high conductivity of heat. The spectra of the arc and spark differ considerably. The brighter lines in the following table are only present in the latter; but Thalén, Huggins, and Hartley and Adeney observed a number of fainter lines, which are also absent from the arc-spectrum.

Spark and arc spectra:

5623.5*	5471.72	5465.66	5209.25	4668.70	4476.29	4212.1	4055.44
3981.87	3383.00	3280.80	3130.09	2938.42	2824.50	2575.70	2375.1
2312.5	2309.74						

SODIUM.

Some of the sodium lines are obtained with extraordinary ease, particularly the *D*-lines and the less refrangible ultra-violet ones. The *D*-lines with a low dispersive power appear as one, and the particles of sodium chloride present in the air are sufficient to cause their production. This fact has exercised some influence on the development of spectrum analysis,

¹ A. B. A. 1861.

² N. A. S. U. (1868) [3] 6.

³ P. T. 1864, p. 139.

⁴ Spectres lumineux (Paris, 1874).

⁵ P. T. (1874) 164, 805.

⁶ *Ibid.* (1884) 175, 109.

⁷ A. B. A. 1892. See also Mascart, Ann. de l'École normale (1866) 4

* Visible only in the spark-spectrum. (Thalén.)

as the universal occurrence of the lines could not be explained until Swan,¹ in 1856, pointed out their origin.

The reversal of the sodium lines was the first observation leading to the formulation of Kirchhoff's law of exchanges, on which spectrum analysis may be said to be based.

Arc and spark spectra:²

8200.3	8188.3	6160.97	6154.43	[D ₁] 5896.16*	[D ₂] 5890.19*
5688.43	5682.86	5153.72	5149.19	4983.53	4979.30
3303.07	3302.47	2852.91	2680.46		

STRONTIUM.

Mitscherlich obtained the line-spectrum by the use of the oxyhydrogen flame; it is also produced by the passage of sparks through a solution of the chloride, but the best effects are given by the volatilization of the chloride in the electric arc. This was the method employed by Kayser and Runge.³ In the Bunsen flame the strontium haloïd compounds chiefly exhibit their individual spectra, together with the band-spectrum of the oxide, and the blue line, $\lambda = 4607.5$, of the metal.

¹ T. R. S. E. (1857) 21.

² Kayser and Runge, A. B. A. 1890. Bunsen and Kirchhoff, P. A. 110, 167. Kirchhoff, A. B. A. 1861. Attfield, P. T. 1862, 221. Rutherford, Silliman's Journ. [2] 35, 407. Huggins, P. T. 1864, p. 139. Wolf and Diacon, C. r. 55, 334. Müller, P. A. 118, 641. Thalén, N. A. S. U. (1868) [3] 6. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Lockyer P. R. S. (1879) 29, 140. Cornu, Spectre normal du soleil (Paris, 1881). Bunsen, P. A. 155, 366. Liveing and Dewar, P. R. S. 28, 367, 471; (1879) 29, 398, 402. E. Becquerel, C. r. 94, 1218; 97, 72. De Gramont, C. r. (1896) 122, 1411, 1443.

³ A. B. A. 1891. See also Bunsen and Kirchhoff, P. A. 110, 167. Kirchhoff, A. B. A. 1861. Müller, P. A. 118, 641. Huggins, P. T. 1864, p. 139. Mascart, Annales de l'École normale (1866) 4. Thalén, N. A. S. U. (1868) [3] 6. Lockyer, P. T. 163, 639; 164, 311. E. Becquerel, C. r. 96, 1218; (1883) 97, 72. Liveing and Dewar, P. T. 174, 217. Rydberg, W. A. (1894) 52, 119.

* Visible also in the flame-spectrum.

Arc and spark spectra:

6550.53	6408.65	6386.74	5543.49	5540.28	5535.01	5522.02
5504.48	5486.37	5481.15	5451.08	5257.12	5238.76	5229.52
5225.35	5222.43	5156.37	4968.11	4962.45	4892.20	4876.35
4872.66	4868.92	4855.27	4832.23	4812.01	4784.43	4742.07
4722.42	4678.39	4607.52*	4531.54	4438.22	4361.87	4338.00
4305.60	4215.66	4161.95	4077.88	4030.45	3705.88	3547.92
4399.40	3475.01	3464.58	3380.89	3366.43	3351.35	3330.15
3322.32	3307.64	3301.81	2931.98			

STRONTIUM CHLORIDE.¹

Flame-spectrum:

6730 6599 6351

STRONTIUM OXIDE.²

Flame-spectrum:

6863.5† 6747.2† 6628† 6499† 6465‡ (6060 6632) **4607.5**

SULPHUR.

Sulphur exhibits both a line- and a band-spectrum; the former was first observed by Seguin,³ who passed sparks through a mixture of hydrogen and sulphur vapor; Plücker and Hittorf⁴ volatilized sulphur in a Geissler tube, and employed sparks from a Leyden jar. This general method is still in use; it suffers from the disadvantage that powerful sparks under a low pressure are apt to decompose any sulphur compounds in the glass, and so give rise to the sulphur-

¹ Mitscherlich, P. A. **121**, 459. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Bunsen, P. A. (1875) **155**, 230.

² Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Eder and Valenta, Denkschriften Wiener Akad. (1893) **60**, 473.

³ C. r. (1861) **53**, 127.

⁴ P. T. **155**, 13.

* Blue line visible also in the flame-spectrum.

† Bands sharply bordered towards the red, shading off towards the violet.

‡ Middle of a band.

spectrum when it is not desired. The band-spectrum is obtained by the passage of feeble sparks through a Geissler tube containing sulphur vapor. Salet¹ produced it by volatilizing sulphur, or one of its compounds, in a hydrogen flame, cooled by allowing it to impinge on a plate of metal or marble, on to the other side of which a stream of water was directed. This spectrum was mapped by Salet, and by Plücker and Hittorf, but the observations are limited to the visible region, and are too inaccurate to show more than the existence of the bands. The flame of burning sulphur exhibits a continuous spectrum which extends far into the violet.

Line-spectrum:

5660.7	5640.3	5604.9	5562.4	5508.3	5471.4	5451.9	5439.0	5430.7
5342.6	5320.1	5215.4	5201.1	5143.3	5103.7	5033.3	5013.5	4994.7
4926.0	4919.4	4902.8	4885.4	4816.6	4715.8	4552.3	4525.5	4485.9
4464.7								

Band-spectrum.² Bands sharply bordered towards the violet, but shading off towards the red (Salet):

5366	5221	5191	5089	5041	4991	4946	4841	4796	4656	4616	4471
------	------	------	------	------	------	------	------	------	------	------	------

TANTALUM.

The lines of this element were too feeble for Thalén to measure, but Lockyer³ observed eighteen of them in the arc-spectrum between $\lambda = 4000$ and 3900 .

TELLURIUM.

The line-spectrum of tellurium is obtained by passing sparks between electrodes of the element, and has been meas-

¹ A. c. p. [4] **28**, 37. C. r. (1869) **68**, 404. See also Hasselberg, Bull. Acad. imp. St. Pétersb. (1880) **11**, 307. Astronomy and Astrophysics (1893), **12**, 347. Mulder, J. pr. Chem. (1864) **91**, 112. Ditte, C. r. **73**, 559. Lockyer, P. R. S. **22**, 374. Gernez, C. r. (1872) **74**, 803. Ångström, P. A. **137**, 300. C. r. **73**, 368. Ciamician, Wien. Ber. **77**, 839; **82**, 425. Schuster, B. A. R. 1880, p. 272. Ames, Astronomy and Astrophysics (1893), **12**. De Gramont, C. r. (1896) **122**, 1326.

² Salet, A. c. p. [4] **28**, 37. C. r. (1874) **79**, 1231.

³ P. T. **173**, 561.

ured by Huggins,¹ and Thalén² in the visible region, and by Hartley and Adeney³ in the ultra-violet. Salet⁴ produced a band-spectrum by passing a discharge through a Geissler tube of hard glass containing tellurium; to facilitate heating, the tube was covered with metal. The spectrum consists of bands in the red, and channelled spaces in the green and blue; they are sharply bordered towards the violet, and shade off towards the red. The same spectrum is produced by volatilizing tellurium in a hydrogen flame. Gernez⁵ investigated the absorption-spectra of tellurium chloride and bromide; they consist of channelled spaces, the former in the green and orange, the latter chiefly in the red and yellow.

Spark-spectrum:

6438.2	6047.2	6013.7	5974.1	5936.2	5782.0	5756.1	5707.6
5648.1	5575.1	5489.1	5478.5	5448.5	5367.1	5311.0	5218.2
5153.1	5104.9	4302.1	4275.0	4260.4	4221.7	4062.0	4054.8
4006.7	3984.5	3969.3	3948.7	3841.9	3736.1	3726.7	(3650.0
3645.1)	3617.8	3552.4	3520.9	3496.9	3456.7	3441.9	3409.2
3384.1	3364.1	3354.6	3331.2	3309.3	(3282.0	3275.3)	3258.2
3248.7	3107.9	3073.1	3046.4	3017.0	2966.5	2941.2	(2894.7
2893.7)	(2868.1	2860.4	2857.4)	(2845.3	2840.4	2823.6)	2792.3
(2769.0	2766.9)	2710.6	(2697.0	2694.5)	2635.1	2544.1	2529.8
2505.6	2499.0	2473.6	(2448.2	2438.4)	(2413.7	2411.8)	(2404.1
2400.4)	(2386.7	2384.2)	2370.7	2359.0	(2332.4	2325.9)	2321.4
2318.2	2295.4	(2281.0	2277.6)	(2266.6	2261.0	2257.0)	2250.4
(2248.4	2247.7)	2243.7	2219.7	(2211.6	2209.9)	(2192.6	2190.1)
2179.6							

THALLIUM.

Thallium salts, heated in the Bunsen flame, exhibit the characteristic green line of wave-length 5350.65. The visible portion of the spark-spectrum has been investigated by

¹ P. T. 1864, p. 139.

² N. A. S. U. (1868) [3] 6 (w.-l. 6438.2-5104.9).

³ P. T. (1883) 175, 63 (w.-l. 4302.1-2179.6).

⁴ A. c. p. [4] 28, 49. C. r. 73, 742. Spectroscopie (Paris, 1888).

⁵ C. r. 74, 1190. See also Ditte, *Ibid.* (1872) 73, 622.

Huggins,¹ and Thalén,² the ultra-violet region by Hartley and Adeney,³ and Cornu.⁴ The arc-spectrum has been measured by Liveing and Dewar,⁵ and more recently by Kayser and Runge,⁶ who usually obtained it from the metal, but occasionally used the chloride; they photographed it between the limits $630\mu\mu$ and $210\mu\mu$. The numerous lines in the spark-spectrum between $650\mu\mu$ and $300\mu\mu$ are almost all absent from the arc-spectrum. With the exception of the green line at $535\mu\mu$, and a faint line at $553\mu\mu$, the rays of thallium, which are powerful, consist wholly of ultra-violet light.

Arc and spark spectra:

5948.7*	5350.65†	5153.6*	5079.4*	5053.9*	4982.5*	4736.5*	4110.2*
3933.4*	3775.87	3529.58	3519.39	3229.88	2921.63	2918.43	2826.27
2767.9†	2709.33	2665.67	2609.08	2580.23	2552.62	2379.66	2316.01
2237.91							

THORIUM.

The spark-spectrum of thorium has been measured by Thalén;⁷ Rowland⁸ records, in his table of wave-lengths, several additional bright lines which he obtained with the arc.

Spark-spectrum:

5538.0	5446.9	5375.5	5350.67†	4919.9	4864.5	4393.2
4382.2	4281.6	4278.1	4273.1	3575.87†	3529.55†	3519.34†

¹ P. T. (1864) **154**, 139.

² N. A. S. U. (1868) [3] **6**.

³ P. T. (1884) **175**, 104.

⁴ C. r. (1885) **100**, 1181.

⁵ P. R. S. **27**, 132. P. T. (1883) **174**, 219.

⁶ A. B. A. 1892. See also W. A. Miller, P. T. (1862) **152**, 861. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Crookes, P. T. **153**, 277. P. M. [4] **26**, 55. Bunsen, P. A. (1875) **155**, 230, 366. Lockyer and Roberts, P. R. S. **23**, 344. Ciamician, Wien. Ber. **76**, 499.

⁷ N. A. S. U. (1868) [3] **6**.

⁸ Astronomy and Astrophysics (1893) **12**, 321.

* Visible only in the spark-spectrum. (Thalén, Hartley and Adeney.)

† Visible also in the flame-spectrum.

‡ In the arc-spectrum. (Rowland.)

THULIUM.

This element was discovered by Clève in 1879, and its spark-spectrum measured by Thalén.¹ The oxide is hardly perceptibly volatile in the Bunsen flame, but exhibits a discontinuous spectrum consisting of the bands $\lambda = 6840$ and 4760 ; the former corresponds with the absorption-bands shown by thulium salts, and Thalén describes an additional one at $\lambda = 4650$. Kruss and Nilson consider that thulium, like other metals of the rare earths, is not an element (comp. didymium).

Spark-spectrum:

5962.5	5897.0	5676.0	5306.6	5034.3	4733.9	4615.8	4522.8
4481.8	4387.2	4360.1	4242.1	4204.6	4188.4	4107.3	4093.7

TIN.

The spark-spectrum is obtained by the use of tin electrodes, or of a concentrated solution of a salt; it has been measured by Kirchhoff,² Huggins,³ Thalén,⁴ and Hartley and Adeney;⁵ the arc-spectrum by Liveing and Dewar,⁶ and Kayser and Runge.⁷ The spectra differ considerably in the visible region, the latter only contains two lines, but four additional ones are included in the spark-spectrum, which also contains more lines in the ultra-violet. Salet⁸ observed a band-spectrum of the oxide, and also a characteristic reddish yellow band at 610μ , when the chloride is volatilized in a hydrogen flame; these results were confirmed by H. W. Vogel.⁹

¹ Öfversigt K. Vetensk. Förhandl. (1881) 40.

² A. B. A. (1861).

³ P. T. (1864) 154, 139.

⁴ N. A. S. U. (1868) [3] 6.

⁵ *Ibid.* (1884) 175, 104.

⁶ P. T. (1883) 174, 219.

⁷ A. B. A. 1893.

⁸ A. c. p. (1873) [4] 28, 68.

⁹ Prakt. Spectralanalyse (Berlin, 1889). See also Mascart, Ann. de l'École normale (1866) 4. Lecoq de Boisbaudran, Spectres lumineux (Paris, 1874). Lockyer and Roberts, P. R. S. (1875) 23, 344.

Spark and arc spectra:

6453.3*	5799.0*	5631.9†	5589.5*	5563.5*	4524.92	3801.16	3745.7†
3595.9†	3352.3†	3330.7†	3283.4†	3262.44	3175.12	3034.21	3009.24
2913.67	2863.41	2850.72	2840.06	2788.09	2779.92	2706.61	2661.35
2658.3†	2643.6†	2631.9†	2594.49	2571.67	2558.12	2546.63	2531.35
2495.80	2483.50	2429.58	2421.78	2408.27	2354.94	2334.89	2317.32
2286.79	2269.03	2267.30	2251.29	2246.15	2231.80	2209.78	2199.46
2194.63	2171.5	2151.2	2148.7	2141.1	2121.5	2113.9	2100.9
2096.4	2091.7	2080.2	2073.0	2068.7	2063.8	2058.3	2053.8

TITANIUM.

The arc and spark spectra of titanium are very rich in lines which, in the visible region, were measured long ago by Thalén,¹ Ångström, Cornu,² and Liveing and Dewar.³ Lockyer⁴ records twenty-four additional lines between $\lambda = 4000$ and 3900, and Cornu twenty-five between $\lambda = 3510$ and 3217. Hasselberg⁵ has recently subjected the arc-spectrum, between D and $\lambda = 3450$, to a thorough investigation. For its production he introduced a fragment of rutile into the hollow of the carbon anode. Rowland has identified many of the solar lines with those of titanium; they are not all given in the list below, but are included in his table of normal lines in Chapter IX.

Arc-spectrum:

6261.3	6258.6	6222.0§	6215.2§	6126.3§	6098.6§	6091.6§	6084.4§
6065.8§	5999.8§	5979.1§	5966.5§	5953.0§	5922.7	5920.0	5899.56
5866.69	5804.45	5786.21	5774.27	5766.56	5762.52	5739.69	5715.30
5714.12	5702.92	5689.70	5680.15	5675.61	5662.37	5648.81	5644.37
5565.70	(5514.78)	5514.58)	5512.72				

¹ N. A. S. U. (1868) [3] 6.² Spectre normal (Paris, 1881). Journ. de l'École polyt. (1883) 52.³ P. R. S. (1881) 32, 402.⁴ P. T. (1881) 173, 561.⁵ Svensk. Vetensk. Akad. Hand. (1895) 28, No. 1. Astrophys. J. (1896) 3, 116; 4, 212.

* Visible only in the spark-spectrum. (Thalén.)

† Visible only in the spark-spectrum. (Hartley and Adeney.)

‡ 3598.9 cor. (Watts.)

§ Visible in the spark-spectrum.

5504.10	5490.38	5488.44	(5482.09	5481.64)	5429.37	5409.81
5369.81	5297.42	5295.95	5283.63	5266.20	5256.01	5252.26
5238.77	5226.70	5225.15	(5224.71	5224.46	5223.80)	5219.88
5210.55	5193.15	5188.87	5173.94	5152.36	5147.63	5145.62
5120.60	5113.64	5087.24	5064.82	5040.12	5038.55	(5036.65
5036.10)	5025.72	5025.00	5023.02	5020.17	5016.32	5014.49
5013.45	5007.42	4999.67	4997.26	4991.24	4989.33	4981.92
4975.52	4928.50	4921.90	4919.99	4913.76	4900.08	4885.25
4870.28	4868.44	4856.18	4841.00	4820.56	4799.95	4792.65
4778.44	4759.44	4758.30	4742.94	4731.33	4723.32	4722.77
4710.34	4698.94	4693.83	4691.50	4682.03	4675.27	4667.76
4656.60	4650.16	4645.36	4640.11	(4639.83	4639.50)	4629.47
4623.24	4617.41	4572.15	4563.94	4555.64	4552.62	4549.79
4548.93	4544.83	4536.25	4536.12	4535.75	4534.97	4534.15
4533.42	4527.48	4522.97	4518.18	4512.88	4501.43	4489.24
4481.41	4475.00	4471.40	4468.65	4465.96	4457.59	4455.48
4453.87	4453.48	4451.07	4449.32	4443.97	4440.49	4434.15
4430.55	4427.28	4426.24	4423.00	4417.88	4417.46	4404.42
4399.92	4395.17	4394.04	4369.82	4338.05	4326.50	4325.30
4321.82	4318.83	4314.95	4314.50	4313.01	4306.07	4302.08
4301.23	4300.73	4300.19	4299.79	4299.38	4298.82	4295.91
4294.28	4291.07	4290.37	4289.23	4287.55	4286.15	4285.15
4282.85	4281.49	4274.73	4263.28	4256.18	4238.00	4186.27
4171.15	4163.80	4159.79	4151.11	4137.39	4127.67	4123.68
4112.86	4082.57	4078.61	4060.42	4055.18	4030.60	4026.64
4024.71	4021.98	4013.72	4009.06	3998.77	3989.92	3982.62
3981.91	3964.40	3962.98	3958.33	3956.45	3948.80	3947.90
3930.02	3926.48	3924.67	3914.45	3913.58	3904.95	3901.13
3900.68	3895.42	3883.02	3882.49	3882.28	3875.44	3873.40
3869.47	3868.56	3866.60	3862.98	3858.26	3853.87	3853.18
3822.16	3786.20	3771.80	3761.46	3759.42	3753.75	3753.00
3741.19	3729.92	3725.28	3724.70	3722.70	3694.58	3690.04
3685.30	3671.82	3669.08	3662.37	3660.75	3659.91	3658.22
3654.72	3653.61	3646.32	3642.82	3641.48	3635.61	3610.29
3599.25	3598.87	3596.17	3547.15	3535.56	3530.53	3510.98
3505.02	3491.20	3477.33				

TUNGSTEN.

The spectrum of this element is obtained by means of sparks from a Leyden jar, and, in the visible region, has been measured by Thalén.¹ In the arc-spectrum Lockyer² observed seven additional lines between $\lambda = 4000$ and 3900 .

¹ N. A. S. U. (1868) [3] 6.² P. T. (1881) 173, 561.

Spark-spectrum:

5734.1	5514.1	5492.6	5224.2	5071.4	5068.9	5053.9
5014.9	5007.9	4888.5	4843.1	4302.6	4295.6	4269.6

URANIUM.

Thalén¹ measured the lines produced by the passage of powerful sparks from a Leyden jar through a solution of the chloride, and Lockyer² observed fifty-six lines in the arc-spectrum between $\lambda = 4000$ and 3900 . The uranium salts exhibit characteristic absorption-spectra, which have been investigated by H. W. Vogel,³ Morton and Bolton,⁴ and Zimmermann;⁵ some of them are shown in the following chapter. The spectra of the uranic and uranous salts differ; the latter consists of a strong double band in the orange, a feebler band in the green, and a broader one in the blue; these are shown when a uranic salt is reduced by means of zinc and hydrochloric acid, and are not affected by the presence of iron, chromium, cobalt, nickel, zinc, or aluminium (Vogel).

Spark-spectrum:

5914.1	5620.1	5580.2	5563.7	5523.1	5510.1	5494.6
5482.5	5480.5	5478.0	5475.5	5385.1	5027.9	4732.0
4724.0	4543.9	4473.4	4394.3	4374.7	4362.7	4341.2

VANADIUM.

Thalén⁶ has measured the spark-spectrum, and Lockyer has mapped fifty lines in the arc-spectrum between $\lambda = 4000$ and 3900 , whilst the region between $\lambda = 4450$ and

¹ N. A. S. U. (1868) [3] 6.

² P. R. S. **27**, 280. P. T. (1881) **173**, 561.

³ Prakt. Spectralanalyse (Berlin, 1889).

⁴ C. N. (1873) **28**, 47, 113, 164, 233, 244, 257, 268.

⁵ Zeitschr. Anal. Chem. **23**, 221. See also Oeffinger, Inaug.-Diss. Tübingen, 1866. Stokes, P. A. Suppl.-Bd. (1854) **4**, 273. Hagenbach, P. A. (1872) **146**, 395.

⁶ N. A. S. U. (1868) [3] 6.

⁷ P. R. S. **27**, 280. P. T. (1881) **173**, 561.

4030 has been examined by Hasselberg¹ in his investigation of the occurrence of vanadium in rutile.

Arc and spark spectra:

6241.7	6120.1	6090.2	6040.2	5726.1	5703.6	5698.6
5669.1	5627.1	5623.6	5415.4	5241.1	5234.2	4881.9
4875.5	4844.1	4594.30	4586.55	4580.59	4577.36	4545.81
4469.87	4462.53	4460.39	4459.92	4452.17	4444.40	4441.90
4438.01	4416.65	4408.65	4408.40	4407.90	4406.85	4400.75
4395.40	4390.15	4384.90	4379.42	4353.05	4341.15	4333.00
4330.15	4271.80	4268.85	4134.60	4128.25	4123.65	4116.65
4115.65	4115.30	4112.00	4109.95	4105.30	4100.00	4095.60
4092.87	4090.70					

YTTERBIUM.

The spark-spectrum of the ytterbia earths has been measured by Thalén;² no absorption-spectrum of the salts is known.

Spark-spectrum:

6221.9	6005.0	5984.4	5837.0	5819.0	5556.6	5476.9
5353.0	5347.4	5345.9	5335.0	4936.0	4786.5	4725.9

YTTRIUM.

The spectrum measured by Thalén³ was obtained by passing powerful sparks through a solution of the chloride. Lockyer⁴ observed twenty-six lines in the arc-spectrum between $\lambda = 4000$ and 3900 . Rowland⁵ considers it possible that yttrium is composed of two substances, he includes the following ultra-violet lines in his table of wavelengths; they were observed by means of the arc: 3950.50, 3774.48, 3710.44, 3633.28, 3611.20, 3602.06, 3600.88, 3584.66, 3549.15. Crookes⁶ has described a phosphorescent spectrum of yttria.

¹ Bishang till Svenska. Vetensk. Akad. Handl. (1897) **22** Afd. I. No. 7; **23**. Afd. I. No. 3. Astrophys. Jour. (1897) **5**, 194; **6**, 22.

² Öfvers. K. Vetensk. Akad. Förhandl. 1881.

³ Om spectra Yttrium, Erbium, Didym Och Lanthan, (Stockholm, 1874).

⁴ P. T. (1881) **173**, 561.

⁵ Astronomy and Astrophysics (1893), **12**, 321. Johns Hopkins Univ. Circulars (1894), **13**, 73. See also Bunsen. P. A. **155**, 366.

⁶ P. T. **174**, 891. A. c. p. [6] **3**, 145. P. R. S. **35**, 262: **38**, 414.

Phosphorescent spectrum of yttria:

Bands : 6676.7 6180.7 **5737.9** 5492.4 5400.5 4825.7 4323.6

Spark-spectrum:

6614.0	6435.5	6191.4	6181.9	6164.5	6150.1	6131.9	6019.5
6009.5	6003.5	5987.4	5663.0	5605.6	5577.1	5545.6	5544.1
5527.5	5521.0	5510.0	5497.0	5480.4	5473.9	5466.9	5403.0
5206.0	5200.5	5123.3	5118.8	5088.3	4881.9	4855.0	4643.8
4527.3	4422.7	4374.6	4309.6	4177.1	4167.7		

ZINC.

The spectrum of zinc has been measured by Kirchhoff,¹ Huggins,² Thalén,³ Lecoq de Boisbaudran, Mascart,⁴ Cornu,⁵ Lockyer,⁶ Liveing and Dewar,⁷ Hartley and Adeney,⁸ Ames,⁹ and Kayser and Runge.¹⁰ The last observers volatilized the metal or chloride in the carbon arc. The spark-spectrum differs considerably from that of the arc, probably on account of the higher temperature of the former.

Spark and arc spectra:

6363.7*	6103.0*	4924.6*	4912.0	4812.2	4810.71	4722.26
4680.38	4630.06	3345.62	3345.13	3303.03	3302.67	3282.42
3075.99	3072.19	3035.93	3018.50	2801.00	2771.05	2770.94
2756.53	2712.60	2684.29	2670.67	2608.65	2582.57	2570.00
2567.99	2558.03	2542.53	2516.00	2491.67	2246.90	2138.3‡
2099.1†	2073.7†	2061.3†	2024.6†			

¹ A. B. A. 1861.

² P. T. (1866) **154**, 139.

³ N. A. S. U. (1868) [3] **6**.

⁴ Ann. de l'École normale (1866) **4**.

⁵ J. de phys. (1881) **10**, 425. C. r. (1885) **100**, 1181.

⁶ P. T. (1873) **163**, 253, 639.

⁷ P. R. S. **29**, 402. P. T. (1883) **174**, 205.

⁸ P. T. **175**, 63.

⁹ P. M. (1890) [5] **30**, 33.

¹⁰ A. B. A. 1891.

* Only in the spark-spectrum (Thalén).

† Only in the spark-spectrum (Cornu).

‡ Only in the spark-spectrum (Ames).

ZIRCONIUM.

The visible portion of the spark-spectrum has been measured by Thalén,¹ who passed powerful sparks through the chloride. Lockyer² observed twenty-three lines in the arc-spectrum between $\lambda = 4000$ and 3900 .

Spark-spectrum:

6344.8	6311.3	6141.8	6133.7	6128.1	5350.5	5191.7
4816.1	4772.1	4739.5	4710.5	4687.5	4155.7	4149.7

¹ N. A. S. U. (1868) [3] 6.

² P. T. (1881) 173, 561. See also Troost and Hautefeuille, C. r. (1871) 73, 620.

CHAPTER VIII.

ABSORPTION-SPECTRA.

AN attempt to treat absorption-spectra in the same systematic manner as emission-spectra is attended with considerable difficulty. The latter have in many cases been thoroughly investigated, and all the lines measured on a uniform system of wave-lengths, but observations of the former are almost exclusively confined to the visible region, although some investigations of the ultra-violet and infra-red regions have given very promising results. Many of the observations have been made by the help of instruments unprovided with measuring appliances, or, when these were present, only arbitrary scales were employed. The majority of observers omit details of the concentration of the solutions, and of the thickness of the layer of liquid, so that the results plotted as curves are not comparable with one another. Krüss' method of determining the minimum of brightness is perhaps well adapted to give results meeting the above conditions, but hitherto it has not been generally employed. Some of the problems which have arisen during the later development of spectroscopic work should be capable of solution by the study of absorption-spectra, but this can only occur if the investigations are conducted on a totally different plan, and the greater portion of the work hitherto accomplished must be repeated.¹

¹ Comp. Hasselberg, K. Svenska Vetensk. Akad. Handl. (1891) 24. No. 3.

These criticisms are not intended to imply that the study of absorption-spectra has been entirely lacking in important results; the weighty and thorough investigations of the solar spectrum which belongs to this class of spectra, and is treated separately in the following chapter, would of themselves be sufficient to prove the contrary. In addition numerous important observations have been made in various other directions; some of those referring to inorganic substances are mentioned in the preceding chapter. In the majority of instances, although the results have some value as preliminary observations, they lack the degree of accuracy attainable at the present time, and are of such unequal value that they can scarcely be included in a work such as this, where detailed criticism would be out of place, whilst the redrawing of curves on a uniform scale instead of the arbitrary ones, would introduce fresh sources of confusion and error.

The account given in the following pages will be restricted to a record of the laws deducible from the results of observations; further details can be obtained by consulting the original memoirs, or H. W. Vogel's "*Praktische spectral-analyse*," Berlin, 1889, which contains numerous illustrations of absorption-spectra.

To show the method usually adopted for the graphic recording of the results, a table of some well-known absorption-spectra is given in Fig. 41. The spectra of inorganic compounds include those of salts of chromium, copper, cobalt, iron, manganese, nickel, and uranium, whilst the organic compounds are alizarin, aniline blue, chlorophyll, eosin, fluorescein, fuchsin (magenta), indigo, malachite green, methyl violet, purpurin, quinoline red, safranin, and blood in aqueous solution, both alone, and after treatment with reagents; these are useful for the identification of blood-stains, and for the diagnosis of carbon monoxide poisoning.

Absorption by Gases and Liquids.—The laws of the absorption by gases have been discussed in Chapter VI. The

TABLE OF ABSORPTION-SPECTRA.

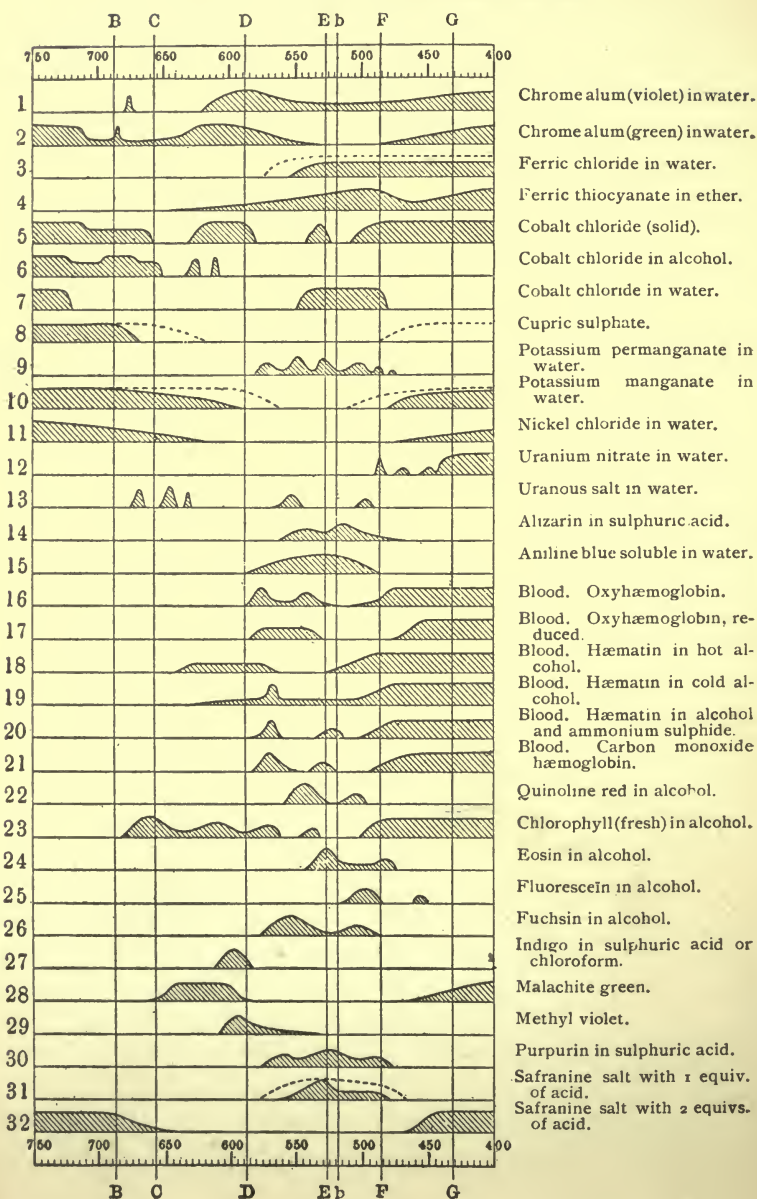


FIG. 41.

absorption by liquids differs, as Ostwald¹ has shown, according to whether or no the substance is a salt. In the case of colored bodies other than salts, the color is a constitutive property, as is well exhibited in the case of organic dyes.² Every change in the molecule produces a definite alteration in the absorptive power, so that variation in the absorption is correlated with change in the molecular condition (Stenger). The absorptive power of salts in dilute solution is purely additive, and is the resultant of the sum of the color of the ions.

Different Salts of the same Colored Base or Acid.—

The first systematic investigations of the absorption-spectra of different salts of the same acid were made by Gladstone;³ his results show that, in general, a base or acid retains its absorptive power in its compounds. Arrhenius' electrolytic dissociation theory indicates that aqueous salt solutions become more dissociated as the dilution increases, until a limit is reached at which the properties become wholly additive, and are the sum of those of the ions. Ostwald has tested this theory by an examination of the color of salt solutions. The absorption-spectrum of a salt, in a solution of infinite concentration, would be rather complex, as the solution would contain at least three constituents, viz., undecomposed molecules, and the two ions; the spectrum would therefore be compounded of three distinct absorption-spectra, the relative intensity of which would be proportional to the quantity of each constituent present, and the undecomposed molecules might exist in aggregations of varying degrees of complexity. With this property, as with all others, increas-

¹ Ueber die Farbe der Ionen. Abhandl. K. säch. Ges. d. Wissensch. 31. Zeitschr. phys. Chem. (1889) 3, 601; (1892) 9, 226, 579. Compare also Maganini, Zeitschr. phys. Chem. 12, 56. O. Knoblauch, W. A. (1891) 43, 738. Wagner, Zeitschr. phys. Chem. 12, 314. Ewan, P. R. S. (1895) 57, 117.

² Stenger, W. A. (1888) 33, 577.

³ P. M. (1857) 14, 418.

ing dilution causes simplification as the molecular aggregates are resolved, until a limit is attained at which the phenomena are caused solely by the ions. The spectrum of a highly dilute salt solution is therefore the sum of the spectra of its ions. The matter may be further simplified by selecting compounds with one colorless ion, i.e., one that exerts no absorptive power on the particular region of wave-lengths under examination. Hence it follows that in highly dilute solutions compounds of a particular colored ion with any colorless ones must give identical absorption-spectra; this is in accordance with Kundt's rule, and apparent exceptions appear to be all due to secondary influences. Ostwald has photographed the absorption-spectra of about 300 salts, including those of the following substances: permanganic acid, fluoresceïn, eosin, iodeosin, tetrabromorcinolphthaleïn, dinitrofluoresceïn, rosolic acid, diazo-resorcinol, diazo-resorufin (resorufin), chromium oxalates, safranines, rosanilines, aniline violet, chrysaniline, and chrysoïdin. All the compounds investigated conformed with the above rule; apparent exceptions were observed in the case of certain feeble acids or bases, the salts of which are hydrolyzed, but the addition of excess of the base or acid overcame this divergence, and the behavior of the solution was then normal. Some salts are insoluble, and therefore not dissociated; these also are apparent exceptions. Occasionally the salt forms visible deposits of a colloïdal nature, but if the dilution prevents this, a determination of the electrolytic conductivity will immediately establish the absence of dissociation.

Relationship between the Molecular Structure and the Absorption-spectrum.—Many investigations have been made to determine the influence of chemical composition on the position of the absorption-bands; a number of regularities have been observed, particularly in the case of organic compounds, but no law of general applicability has been formulated.

Absorption in the Visible Portion of the Spectrum.—

The primary object of the earlier workers was the general investigation of the spectra, rather than their relationship to the chemical constitution of the compounds. The chrysoïdins were the first dyes, the color of which could be changed at will from pale yellow to red by the systematic introduction of various groups; these, and other azo-dyes of known constitution, were examined by Landauer;¹ the spectra obtained were not very sharp, but it was shown that the absorption-bands undergo a marked change when the hydrogen in the amido-group is replaced by methyl. G. Krüss investigated indigo² and fluoresceïn³ derivatives, and arrived at the following conclusions. The substitution of hydrogen by methyl, ethyl, methoxyl, carboxyl, or any group which increases the percentage of carbon in the compound, causes the absorption-bands to approach the red; the effect of bromine is similar. The minima of brightness approximate towards the blue if hydrogen is replaced by the nitro- or amido-groups; the displacement increases as the number of substituting groups rises, and, if the groups are identical, it is proportional to their number. Krüss' rule, except the proportional displacement, was confirmed by Liebermann and Kostanecki⁴ in the case of methylated hydroxyanthraquinones, and by Bernthsen and Goske⁵ in that of dimethyl- and diethylthionine. The latter workers observed that the introduction of two methyl groups produces a displacement of about $20\mu\mu$, the change caused by two additional methyl groups being about $45\mu\mu$. E. Vogel⁶ subsequently proved that the proportional displacement of the absorption-bands is the exception instead of the

¹ Ber. (1881) **14**, 391.

² G. Krüss and S. Oeconomides, *Ibid.* (1883) **16**, 2051.

³ *Ibid.* (1885) **18**, 1426.

⁴ *Ibid.* (1886) **19**, 2327.

⁵ *Ibid.* (1887) **20**, 924. See also Bernthsen, *Studium in der Methyleneblaugruppe*. Lieb. Ann. (1885) **230**, 73. Goske, *Inaug.-Diss.* Zurich, 1887.

⁶ W. A. (1891) **43**, 449.

rule; in the eosin compounds the displacement depends both on the number and position of the substituting groups. In aqueous solution the displacement varies according to whether the substituting group enters the phthalic acid, or the resorcinol nucleus. Influence is also exercised by the position, in the phthalic acid radicle, of the substituting group, if any, and also by the solvent employed. H. W. Vogel¹ had previously shown that the extent to which the absorption-bands are displaced is intimately related to the position of the substituting group in the molecule. He investigated methylated azo-dyes in concentrated sulphuric acid solution. Grebe² worked on the same subject, and examined more than a hundred azo-dyes; his conclusions are as follows: In sulphuric acid solution the absorption-bands of the azo-dyes approach the red as the content of carbon increases. Hydroxyl- and amido-groups act in a similar manner; constancy in the position of the radicles produces a constant displacement of the bands; thus if hydroxyl is introduced into the naphthalene molecule, the α -compounds exhibit bands which are always about $20\mu\mu$ nearer to the red than those of the isomeric β -derivatives. The sulphonic group produces a displacement in the opposite direction; it is almost constant, and approximates to $40\mu\mu$; the bands are more clearly defined, and the influence of the position of the group is also nearly constant.

In connection with the relationship between color and absorption-spectrum Schütze's³ theory of dyes may be mentioned. A study of physics shows that the mixture of colors composing the solar spectrum appears white because each color has an equally strong complementary color; these neutralize one another, and produce on the eye the effect of whiteness. If a color is abstracted from the spectrum by

¹ Sitzungsber. Berl. Akad. (1887) **34**, 715. Ber. **21**, 776c.

² Zeitschr. f. phys. Chem. (1893) **10**, 673. Ber. (1893) **26**, 130c.

³ Zeitschr. f. phys. Chem. (1892) **9**, 109. Meyer's Jahrb. 1892, p. 11.

absorption, the issuing light will be tinged with the complementary color. Many colorless substances exhibit absorption-bands in the ultra-violet; the introduction of groups which displace the bands towards the red ("catho-chromic groups") first produces absorption in the violet, and the substance consequently assumes a greenish yellow color. "Hypsochromic groups" displace the absorption-bands towards the violet, and their introduction causes the opposite effect; such groups are not numerous. This explanation is in accord with the empirical rule, enunciated in 1877 by Nietzki, which states that the simplest dyes are greenish yellow or yellow; as the molecular weight increases, the color changes successively to orange, red, violet, blue, and green. In the case of analogous elements a rise in the atomic weight also produces an increase in the depth of the color; an example is furnished by the fluorine group: this element is light greenish yellow, chlorine is a deeper greenish yellow, bromine red, and iodine violet. Experience shows that the color of many organic compounds is dependent on the presence in the molecule of certain groups, such as the azo-group in the azo-dyes; this suggests that these complexes are probably the active agents in producing the absorption of light by the molecule, and that change in the color caused by substitution is due to influence exerted by the substituting radicles on these groups.¹ This view was first developed by O. N. Witt,² who applied the term "chromophore" to the group producing the color; since the influence of a substituting group on the chromophore will be stronger the nearer their positions approximate in the molecule, the theory affords a prospect of determining the relative distance of the groups by spectroscopic measurement. Schütze examined certain azo-dyes, and found that the relative distance of the atoms in the molecule indicated by the structural

¹ Compare Hartley, *J. Chem. Socy.* (1887) **51**, 152. *Ber.* (1887) **20**, 131.

² *Ibid.* (1876) **9**, 522.

formulae of the compounds corresponded, on the whole, with the spectroscopic measurements.

Spring,¹ using extremely thick layers, observed that "colorless" organic compounds exhibit spectra free from absorption-bands if their molecules consist of carbon chains about which the heterologous atoms or groups are equally or symmetrically divided. Concentration of the atoms or radicles at one end of the chain causes the appearance of absorption-bands. The number of the bands appears to be directly related to the number of the hydrocarbon radicles present in the compound; their position is apparently determined by the nature of each group, but if two of these are very intimately linked, the combined influence causes a change in the position of the corresponding bands, which may even merge into a single one.

Absorption in the Ultra-violet.—The relationship between the constitution of substances and their absorption-spectra in the ultra-violet region was first shown by Soret and Rilliet,² and Hartley and Huntington.³ The former examined the ethylic, isobutylic, and amylic salts of nitric and nitrous acids; these compounds are not well suited to investigations of this nature, as the absorption is confined to one end of the spectrum, and does not include measurable bands, but their observations rendered it probable that the whole absorption-field is displaced towards the red if a hydrogen atom is replaced by methyl. Hartley and Huntington³ obtained more definite results, showing that the normal fatty acids have a stronger absorptive power for the refractive rays of the ultra-violet region than the corresponding alcohols, and that increase in absorptive power in this part of the spectrum is correlated with increase in the number of CH₂ groups in the molecule of the homologous alcohols and acids.

¹ Bull. Acad. roy. Belgique [3] 33, 165. Chem. Centralbl. (1897) 68, 1114.

² C. r. (1879) 89, 747.

³ P. R. S. (1879) p. 233. P. T. (1879) 170, 257.

Hartley,¹ partly in conjunction with Huntington,² has carried out further extensive investigations of the relationship between the absorption-spectra of carbon compounds and their molecular structure. The following is a summary of the results: The alcohols C_nH_{2n+2} , ethers, and ethereal salts (esters) readily transmit the ultra-violet rays; methyl alcohol almost as completely as water; but the fatty acids absorb these rays to a greater extent than do the corresponding alcohols. None of the compounds examined exhibit absorption-bands. In the case of the alcohols and acids the absorption increases as the content of carbon in the compound rises.

Benzene and its hydroxyl-, carboxyl-, and amido-derivatives have a high absorptive power for the ultra-violet rays, and in thin layers exhibit strong absorption-bands. The spectra of isomers differ both in the position of the bands and in the extent of absorption. In the cresols and dihydroxybenzenes the meta-derivative has the greatest, and the para-compound the least absorptive power, but orthoxylene and parahydroxybenzoic acid absorb more light than the isomeric compounds. The spectra of isomeric terpenes differ; the compounds $C_{10}H_{16}$ and $C_{16}H_{24}$ exceed benzene in absorptive power, the former to a greater extent than the latter. Absorption-bands are confined to compounds containing benzenoid carbon linkages. A simple linkage of carbon and nitrogen is insufficient to produce characteristic absorption of the ultra-violet rays. The substitution of a nitrogen atom for a CH group in benzene or naphthalene derivatives (pyridine or quinoline compounds) does not destroy the selective absorption-power, but this disappears if the benzenoid linkage is destroyed by combination with hydrogen. The addition of four atoms of hydrogen to carbon atoms in the quinoline

¹ J. Chem. Socy. (1882); (1885) **47**, 685; (1887) **51**, 58; **53**, 641. Ber. (1885) **18**, 592; (1887) **20**, 174; (1888) **21**, 689.

² P. R. S. **28**, 233; (1879) **29**, 290; (1880) **31**, 1. P. T. (1879) **170**, 257. Ber. (1881) **14**, 501.

molecule only diminishes the intensity of the absorption-bands.

Molecules consisting of dissimilar parts vibrate as wholes. The fundamental vibrations produce secondary, ones which do not bear any recognizable relationship to the chemical constituents.

Hartley has also examined the carbohydrates and albuminoids, and has investigated the physical connection of these compounds with the soluble ferments. The spectra of egg albumin, serum albumin, and casein exhibit certain bands in common which are absent in the spectra of malt diastase, yeast invertase, gelatin, starch, glycoses, and saccharose, solutions of which are particularly transparent to the violet and ultra-violet rays. The albumins are thus shown to differ considerably from the ferments in constitution, and this accords with the difference in behavior shown by the compounds towards carbohydrates.

Absorption in the Infra-red.—The influence of the atomic grouping of organic compounds on their absorption of the infra-red rays has been extensively investigated by Abney and Festing.¹ Hydrogen chloride shows a few lines, water lines and bands; ammonia, and nitric acid sharp lines. Many of these lines coincide, and can be referred to hydrogen. It is to some extent an open question why the hydrogen acts as if it were free, and produces a line-spectrum, but certain absorption-lines exhibited by hydrocarbons are coincident with some shown by compounds of hydrogen and oxygen, or hydrogen and nitrogen, which are known to be due to hydrogen. The behavior of oxygen varies according to whether it is in the radicle; if it links radicles, it produces a continuous absorption between two hydrogen lines. Oxygen in the radicle increases the sharpness of the bands, and causes them to be bordered by lines.

¹ P. R. S. 31, 416; (1881) 32, 258.

Organic radicles are characterized by well-marked bands which chiefly occur between about $700\mu\mu$ and $1000\mu\mu$; some have a distinct absorption at about $700\mu\mu$, and a second in the neighborhood of $900\mu\mu$, but the characteristic absorption of the radicle is almost always in the former region. The ethyl group has an absorption at $742\mu\mu$, and a characteristic band between $892\mu\mu$ and $920\mu\mu$. The characteristic line of the phenyl group is at $867\mu\mu$. A comparison of the spectra of ammonia, benzene, aniline, and dimethylaniline shows a very close coincidence, and proves how slight an effect is produced by varying the mass of the radicles linked to the nitrogen atom. Abney and Festing were unable to demonstrate the presence of haloïds in organic compounds by means of their absorption-spectra in the infra-red.

CHAPTER IX.

THE SOLAR SPECTRUM.

The Fraunhofer Lines.—The solar spectrum is the most complex of all absorption-spectra. It is permeated with a number of vertical lines which were first observed by Wollaston¹ in 1802, and investigated by Fraunhofer,² after whom they are named. He prepared a drawing of the spectrum, which is reproduced in Fig. 42, and contains about 350 lines. The more prominent are designated by the Latin letters *A* to *H*. By means of accurate measurements Fraunhofer showed that the lines are constant both in relative position in the spectrum, and also in mutual distance. He observed that the spectra of the moon and planets are identical with that of the sun, but differ from those of Sirius and other fixed stars, so that the lines must originate in the sun and fixed stars, and not in the earth's atmosphere. In 1824 he proved the coincidence of the double *D*-line of the solar spectrum with that of the sodium-spectrum, but was unable to explain the origin of the dark lines. Nine years later Brewster³ found that when the sun is low, so that the light traverses a considerable thickness of atmosphere, new lines become visible; these are produced by atmospheric absorption, and were first accurately mapped by Brewster⁴ alone, and in conjunction with Gladstone.⁵ Ångström and others almost succeeded

¹ P. T. 1802, p. 365.

² Denkschr. d. Münchener Akad. 1814-15.

³ P. T. E. 1833.

⁴ P. M. [3] 8, 384. P. A. (1836) 38, 50.

⁵ P. T. (1860) 150, 149

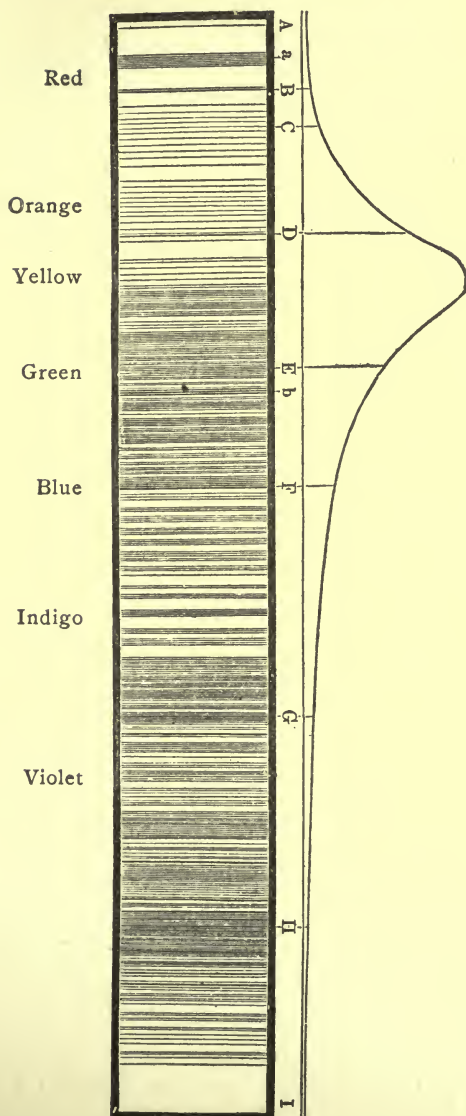


FIG. 42.

in showing the origin of the lines, and this was finally accomplished by Kirchhoff¹ in 1859, as a consequence of the law of exchanges which he had recently formulated (comp. Chapter VI). The explanation of their origin offered a prospect of determining the composition of the sun and fixed stars, so that they at once received considerable attention. It became necessary, therefore, to measure the position of the Fraunhofer lines, and also those in the spectra of the elements, with a greater degree of accuracy than had been hitherto attained; this was done by Kirchhoff,² who used a prism spectroscope, and consequently an arbitrary scale. Ångström, in the preparation of his atlas of the solar spectrum which appeared in 1868, made the measurements in wave-lengths, and, like Fraunhofer, employed diffraction gratings. His normal spectrum included about 1000 lines, all based upon wave-lengths, and the atlas remained the foundation of all wave-length determinations for more than twenty years. The accuracy of his work was scarcely exceeded by the more extensive charts of H. C. Vogel and Müller,³ Fiévez,⁴ Piazzzi-Smyth,⁵ Thollon,⁶ and Young. Mascart,⁷ Draper,⁸ and Cornu⁹ have investigated the ultra-violet region of the solar spectrum; the scale of the chart and the wave-lengths of the last observer correspond with those of Ångström. Abney¹⁰ photographed the infra-red region, and used his own special plates, which are sensitive to

¹ Monatsber. Berl. Akad. V. 27, Oct. 1859.

² A. B. A. 1861.

³ Publicationen des Astrophys. Obs. zu Potsdam (1879), 1.

⁴ Annales de l'Observatoire Royal de Bruxelles (1882) [3], 4; (1883) 5.

⁵ T. R. S. E. (1880) 29, 285; 32, 37, 233, 519.

⁶ C. r. 88, 80. Ann. de l'Observ. de Nice (1890), 3.

⁷ Ann. de l'École normale sup. (1864) 1.

⁸ Sillim. Jour. 1873. P. A. (1874) 151.

⁹ C. r. 86, 101, 315, 530. Ann. de l'École norm. [2] 3, 421; 9, 21. Spectre normal du soleil (Paris, 1881).

¹⁰ P. M. [5] 6, 154; 11, 300. P. T. (1880) 171, 653; (1886) 177. W. A. Beibl. 4, 375; 5, 507, 509. Abney and Festing, P. R. S. 35, 80, 324. W. A. Beibl. 8, 507.

these rays. The spectrum was at first obtained by means of prisms, but subsequently with a Rowland's concave grating. Lommel¹ has also photographed the infra-red Fraunhofer lines, and Langley² has investigated them by means of the bolometer (comp. Chapter V). Mascart and Cornu extended Fraunhofer's designation of the lines by Latin capitals up to $U = 2948$ Ångströms, and Abney introduced the following signs for the infra-red:

Ψ_2	} 27000	Y	{ 8990.4 8986.5	X_2	8541.8 8497.0	} Calculated on Ångström's scale.	
Ψ_1							
Φ_2	12400	X_4	8806.1	Z	8226.4		
Φ_1	12000	X_3	8661.4				

After Ångström's death it was found that his determinations were about $\frac{1}{8000}$ too small in consequence of his having used an incorrect metre-scale, so that new and more exact wave-length measurements became necessary. Müller and Kempf³ made careful investigation of 300 solar lines, and almost simultaneously Rowland, in 1886, published the first edition of his photographic atlas of the normal solar spectrum. A superior and more complete edition⁴ appeared in 1889. It consists of ten tables, each measuring 3×2 feet, and containing two spectrum sections. It includes the region between 3000 and 6950 Ångströms, and the scale which is attached is correct to within less than 0.05 Ångström. Photographs which are made by the sun itself are obviously superior to charts prepared by drawing and measurements. As an appendix to the atlas, Rowland⁵ has published a table of the wave-lengths of numerous solar and metallic lines, the results of ten years' observations; they have been determined by his coinci-

¹ Comp. Chap. V.

² Sillim. Journ. [3] 25; 28; 31; (1886) 32; (1888) 36; (1889) 38. W. A. (1883) 19, 226, 384; (1884) 22. Beibl. 9, 335.

³ Publicat. d. Astrophys. Obs. zu Potsdam (1886) 5.

⁴ Photographic map of the normal solar spectrum. Baltimore, Md., Johns Hopkins Press. The price of the tables is \$2.50, or \$20 the set.

⁵ Astronomy and Astrophysics (1893), 12, 321. P. M. (1894) [5] 36, 49.

dence method, and are exact within 0.01 Ångström; in many instances the accuracy is within 0.001 Ångström, i.e., 1 in 5,000,000.¹ The value $D_1 = 5896.156$ is taken by Rowland as the basis of his tables (comp. Chapter VII).

An exact knowledge of the position of the solar lines is of the greatest importance for the orientation of spectra, and for the determination of the constituents of the sun; therefore in the following table Rowland's measurements of the Fraunhofer lines are reproduced in full. The letter preceding a line is the one in general use for its designation; chemical symbols following it indicate the element with a line of which it coincides. A query (?) after the symbol means that it is doubtful whether the line does belong to the spectrum of the element. Two symbols after a line, such as 3295.957 Mn-Di, implies that both elements have a coincident line of this wavelength. Two or more symbols in brackets show that a line of the first element corresponds with one side of the solar line, one of the second with its middle, etc. Lines which do not coincide with those of any known element are followed by a query, whilst those due to absorption by atmospheric oxygen or moisture are designated by atm. (O) or atm. (H₂O). All the wave-lengths are given in Ångström units, reduced to air at 20° C., under a pressure of 760 mm.

The Chemical Composition of the Sun.—The establishment of Kirchhoff's law, and the experimental reversal of the sodium lines (comp. Chapter VI) naturally directed attention to the elucidation of the composition of the sun. Kirchhoff's careful drawings of spectra were prepared for the purpose of comparing the position of solar and metal lines. He employed the Fraunhofer lines for the orientation of metallic lines, and found that the iron lines coincided exactly with similar dark lines. That the coincidence of only sixty lines should be a

¹ A list of the lines in Rowland's tables has appeared in the *Astrophys. Jour.* from 1895 onwards.

ROWLAND'S TABLE OF WAVE-LENGTHS OF THE FRAUNHOFER LINES.

Based on $D_1 = 5876.156$ Ångströms, and reduced to air at 20° and 760 mm. pressure.

3005.160	?	3134.223	Ni				
3005.404	?	3137.441	Co		3377.667	Ti }	
3012.557	?	3140.869	Fe		3389.887	Ti }	
3014.274	?	3153.870	Fe			Co }	
3016.296	Fe	3158.988	Ca		3405.272	Ti }	
3024.475	?	3167.290	Mn		3406.581	Fe	
3025.394	?	3172.175	Fe?		3406.955	Fe	
3025.958	Fe	3176.104	La?		3425.721	?	
3035.850	?	3188.164	Cr?		3427.282	Fe	
3037.492	Fe	3195.702	Ni		3440.759	Fe	
3044.119	Ca[?Co]	3200.032	Ti	[O]	3441.135	Fe	
3044.683	Mn	3214.152	Fe		3444.032	Fe	
3046.778	?	3218.390	Ti		3455.384	Co	
3047.720	Fe	3219.697	Fe		3464.609	Sr?	
3050.212	?	3219.909	Fe			Co }	
3053.173	Fe		Fe? }		3465.991	Fe }	
3053.527	?	3222.203	?		3475.594	Fe	
3055.821	?	3224.368	Ti		3476.831	Fe	
3057.557	Fe	3225.923	Fe			Co }	
3059.200	Fe		Ti }		3478.001	Fe }	
3061.098	?	3231.421	?			Ni }	
3061.930	Co	3232.404	Ti		3486.036	Ni	
3067.363	Fe	3236.697	Ti		3490.721	Fe	
3075.339	Ti		?		3491.464	Co }	
3075.849	Fe	3246.124	Fe }			?	
3077.216	Fe	3247.680	Cu		3497.264	Fe	
3077.303	?		Mn }		3497.991	Fe }	
3078.148	Fe?	3260.384	Fe }			?	
3078.759	Ti		Fe }		3500.721	Fe	
3079.724	Mn	3267.839	V		3500.993	Ni	
3080.863	?	3274.092	Cu		3510.987	Ti	
3082.272	Al	3287.791	Ti		3513.947	Fe	
3083.849	Fe		Fe }		3518.487	Co	
3086.891	?	3292.174	Co-T }		3521.404	Fe	
3088.137	Ti	3295.957	Mn-Di		3540.266	Fe	
3092.824	Al	3302.501	Na		3545.333	?	
3092.962	Al	3303.107	Na		3549.145	Yt	
3094.739	?		?		3550.006	Fe	
3095.003	Fe	3303.648	Fe }		3558.670	Fe	
3100.064	Fe	3306.117	Fe			Ti }	
3100.415	Fe(Mn)	3306.471	Fe		3564.680	Fe }	
3100.779	Fe		Mn }		3565.528	Fe	
3101.673	Ni	3308.928	Co-Ti }		3570.225	Fe	
3101.994	Ni	3318.163	Ti		3570.402	Fe	
3106.677	?	3331.741	Fe	[N]	3581.344	Fe	
3109.434	Cr?		Cr }		3583.483	Fe?	
3115.160	Fe	3348.011	Fe }		3584.662	Yt	
3121.275	V	3351.877	Fe		3585.992	C	
3129.882	Zr	3356.222	Zr		3586.041	C	

ROWLAND'S TABLE.—Continued.

3590.523	C	3736.969	Ni }	3883.773	Cr
3597.192	Fe		Mn }	3886.427	Fe
3600.880	Yt(Fe)	3737.075	Ca	3897.599	Fe
3602.061	Yt	3737.282	Fe	3905.666	Si
3605.483	Cr		Ti }	3916.875	Fe
3605.635	Fe	3743.502	Fe }	3924.669	Ti
3606.831	Fe		Cr }		Fe }
3609.015	Fe	3745.701	Fe	3925.345	V }
3611.193	Yt	3746.054	Fe	3925.792	Fe
3612.217	Fe		Fe }		Fe }
	Ca }	3747.095	? }	3926.123	? }
3617.920	Fe }	3748.409	Fe	3928.071	Fe
3618.924	Fe	3749.633	Fe	[K] 3933.809	Ca
3621.122	Yt		? }	3937.474	Fe
3621.606	Fe	3754.664	? }	3941.021	Fe-Co
3622.147	Fe	3756.211	Fe		? }
3623.332	Fe	3758.379	Fe	3942.559	Fe }
3623.603	Fe	3763.942	Fe	3944.159	Al
3628.853	Yt	3767.344	Fe	3949.034	Ca
3631.619	Fe	3770.130	Fe	3950.101	Fe
3633.259	Yt	3774.480	Yt?	3950.497	Yt
3635.616	Ti	3780.846	?	3954.001	Fe
3638.435	Fe	3781.330	Fe	3957.180	Fe-Ca
	Cr }	3783.074	Ni	3960.429	Fe
3640.536	Fe }	3788.032	Fe	3961.676	Al
3647.995	Fe	3794.014	Fe-Cr	[H] 3968.620	Ca
3652.692	Co	3795.150	Fe	3971.478	Fe
3653.639	Ti	3798.662	Fe	3973.835	Ca
	Mn }	3799.698	Fe	3977.891	Fe
3658.688	Fe }	3804.153	Fe	3981.914	Fe-Ti
3667.397	Fe	3805.487	Fe-Di		Cr }
3680.064	Fe	[L] 3815.985	Fe	3984.078	Fe }
	Co }	3820.567	Fe		? }
	V }	3821.318	Fe	3986.903	Mn }
3683.202	Fe }	3823.651	Mn(Cr)		? }
	Pb	3826.024	Fe	3987.216	Mn }
3683.622	Fe	3827.973	Fe		Co }
3684.259	Fe	3829.505	Mg	4003.916	Ce-Fe-Ti
3687.607	Yt	3832.446	Mg	4005.305	Fe-?
3694.349	Fe	3836.226	?-C	4016.578	Fe
3695.194	Fe	3836.652	C		Fe }
3705.711	Fe	3838.430	Mg	4029.796	Zr }
3707.186	Fe	3840.584	Fe	4030.914	Mn
3709.397	Yt	3843.406	Fe	4033.225	Mn
3710.438	Fe	3856.517	Fe	4034.641	Mn
3716.585	Fe	3860.048	Fe	4035.88	Mn
3720.086	Ni }	3864.441	C	4044.293	K
	Fe-Ti }	3871.528	C	4045.975	Fe
3722.691	Fe		? }		Zr }
[M] 3727.763	Fe	3875.224	V }	4048.893	Mn }
3732.542	Fe		C		Cr }
3733.467	Fe	3883.472	C		Mn
3735.014	Fe	3883.548	C	4055.701	

ROWLAND'S TABLE.—Continued.

4062.602	Fe		Ni }		Ti }
4063.756	Fe	4359.778	Cr }	4691.581	Fe }
4071.904	Fe		Zr }	4703.180	Mg
4073.920	Fe	4369.943	Fe	4703.986	Ni
4077.883	Sr	4376.103	Fe	4714.599	Ni
4083.767	Fe }	[d] 4383.721	Fe	4722.349	Zn
	Mn }		Fe }		Fe }
4083.928	Fe	4391.149	Ti }	4727.628	Mn }
4088.716	Fe	4404.927	Fe	4754.226	Mn
	Si }		V }	4783.601	Mn
4103.121	Mn }	4407.850	Fe }		? }
4107.646	Fe	4413.181	Cd	4805.253	Ti }
4114.600	Fe	4415.299	Fe	4810.723	Zn
	Cr }	4425.609	Ca	4823.697	Mn
4121.481	Co }	4435.132	Ca	4824.325	Fe?
4121.968	Fe-Cr	4435.852	Ca	4859.934	Fe
4157.948	Fe	4447.899	Fe	[F] 4861.496	H
4185.063	Fe	4454.950	Ca	4890.945	Fe
4197.251	C	4456.047	Ca	4900.098	Ti
	Zr }	4456.793	Ca	4900.306	Yt
4199.263	Fe }	4494.735	Fe		Cr }
4202.188	Fe		Cr }	4903.488	Fe }
4215.616	Fe }	4497.041	Zr }	4919.183	Fe
4215.667		4499.070	Mn }	4920.682	Fe
4215.687	Sr }	4499.315	? }	4924.109	Fe
4216.137	C	4501.444	Ti	4924.955	Fe
4222.381	Fe	4508.456	Ti?	4934.247	Ba
[g] 4226.892	Ca	4554.213	Ba	4957.482	Fe
4250.290	Fe	4563.939	Ti	4957.786	Fe
4250.956	Fe	4571.277	Mg		Ti }
4254.502	Cr	4572.157	Ti	4973.274	Fe }
4260.638	Fe	4578.731	Ca-Ti		? }
	? }	4588.384	Cr?	4978.782	Fe }
4267.958	Fe }	4590.129	Ti?		Ni }
4271.924	Fe	4602.183	Fe	4980.362	? }
4274.958	Cr	4607.509	Sr	4981.915	Ti
4283.170	Ca		? }	4994.316	Fe
4289.523	Ca	4611.453	Fe }	4999.693	Ti-La
4289.881	Cr		Ti }	5005.904	Fe
4293.249	?	4629.515	Co }	5006.303	Fe
4299.152	Ca	4637.683	Fe		Ti }
4302.689	Ca	4638.194	Fe	5007.431	Fe }
4305.636	Sr	4643.645	Fe		(Ni)Ti }
4306.071	Ti	4648.835	Ni	5014.422	Ti }
4307.904	Ca }		? }	5020.210	Ti
[G] 4308.034		4668.303	Fe }		Ti }
4308.071	Fe }	4678.353	Cd	5036.113	Ni }
4318.818	Ca	4679.028	Fe	5041.795	Ca
[f] 4325.940	Fe	4680.319	Zn	5050.008	Fe
	Cr }	4683.743	Fe	5060.252	Fe
4343.387	Fe }	4686.395	Ni	5064.833	Ti
4352.903	Fe	4690.324	?	5068.946	Fe

ROWLAND'S TABLE.—Continued.

5083.525	Fe	5217.559	Fe	5383.576	Fe
5090.959	Fe	5225.690	Fe	5389.683	Fe
5097.176	Fe	5230.014	Fe	5393.378	Fe
5105.719	Fe(Cu)	5233.124	Fe	5397.346	Fe
5109.825	Fe	5242.662	Fe	5405.987	Fe
5110.570	?	5250.391	Fe	5410.000	Cr
5115.558	Fe }	5250.825	Fe	5415.421	Fe }
5121.797	Ni }	5253.649	Fe		V }
	Ni }	5260.557	Ca		V }
5126.369	Fe }	5261.880	Ca }	5424.284	Fe }
5127.530	Co		Cr }	5434.742	Fe
	Fe	5262.341	?	5447.130	Fe
5133.871	Fe }	5262.391	Ca }	5455.666	Fe? }
	?	5264.327	Cr }	5455.759	
5139.437	Fe }	5264.371		5455.826	Fe }
5139.539		5264.395	Ca }	5462.732	Ni
5139.645	Fe	5265.727	Ca }	5463.174	Fe
5141.916	Fe	5265.789		5463.493	Fe
5142.967	Ni }		(Ni?)	5466.608	Fe
5143.042		5265.884	Cr }	5477.128	Ni
5143.106	Fe }		Fe	5487.968	Fe
	Ni }	[E ₂] 5269.722	Fe	5497.731	Fe
5146.664	?	5270.448	Ca }	5501.685	Fe
	Fe }	[E ₁] 5270.495		5507.000	Fe
5151.026	Mn }	5270.533	Fe }	5513.207	Ca
5154.237	Ti? Co?	5273.344	Fe }	5528.636	Mg
5155.937	Ni	5273.443		5535.073	Fe
5159.240	Fe?	5273.554	Fe }	5543.418	Fe
5162.448	Fe		?	5544.158	Fe
5165.190	C	5276.205	Cr }	5555.113	Fe
5165.588	Fe		Co }	5569.848	Fe
5167.501	Mg }	5281.968	Fe	5576.319	Fe
[b ₄] 5167.572		5283.803	Fe	5582.195	Ca
5167.686	Fe }	5288.708	Fe	5588.980	Ca
5169.066	Fe }	5296.873	Cr	5590.342	Ca
[b ₃] 5169.161		5300.918	Cr	5594.695	Ca
5169.218	Fe }	5307.546	Fe	5598.555	Fe
5171.783	Fe	5316.790	Fe? }	5598.715	Ca
[b ₂] 5172.871	Mg	[1474] 5316.870		5601.501	Ca
5173.912	Ti	5316.950	Co? }		Fe }
[b ₁] 5183.792	Mg	5324.373	Fe	5603.097	Ca }
5188.863	Ti }	5333.092	Fe?		Fe }
5188.948		5349.623	Ca	5615.526	Fe
5189.020	Ca }	5353.592	Fe-Ni	5615.879	Fe
5193.139	Ti	5361.813	?	5624.253	Fe
5198.885	Fe	5363.011	Fe(Co) }	5624.768	Fe-V
	?	5363.056	?	5634.167	Fe
5202.483	Fe }	5367.670	Fe	5641.661	Fe
	Cr }	5370.165	Fe	5645.835	Si
5204.708	Fe }		Ni }	5655.707	Fe
5210.556	Ti	5371.686	Fe-Cr }	5658.096	Yt?
5215.352	Fe	5379.776	Fe	5662.745	Fe

ROWLAND'S TABLE.—Continued.

5675.648	Ti	5930.410	Fe	6256.574	Ni }
5679.249	Fe	5934.883	Fe		Fe }
5682.861	Na	5948.761	Si	6261.316	Ti
5688.434	Na	5956.925	Fe	6265.347	Fe
5701.769	Fe	5975.576	Fe	6270.439	Fe
5708.620	Si	5977.005	Fe	[α] 6278.289	atm. (O)
5709.616	Fe	5977.254	atm. (H ₂ O)	6281.374	atm. (O)
5709.760	Ni	5985.044	Fe	6289.608	atm. (O)
5711.318	Mg	5987.286	Fe	6293.152	atm. (O)
	Ni }	6003.245	Fe	6296.144	atm. (O)
5715.309	Fe-Ti }	6008.196	Fe	6301.719	Fe
5731.973	Fe	6008.782	Fe	6314.874	Ni
5742.066	Fe	6013.717	Mn	6315.541	Fe
5752.257	Fe	6016.856	Mn	6318.242	Fe-(Ca)
5753.342	Fe		? }	6322.912	Fe
	Ni }	6020.347	Fe }	6335.550	Fe
5754.884	? }	6022.017	Mn	6337.042	Fe
5763.215	Fe	6024.280	Fe	6344.370	Fe
5772.360	Si	6027.265	Fe	6355.259	Fe
5775.304	Fe	6042.316	Fe	6358.902	Fe
5782.346	Cu? Co?	6056.232	Fe	6378.461	Ni
5784.081	Cr	6065.708	Fe	6380.951	Fe
5788.136	Cr	6078.709	Fe	6393.818	Fe
	Cr }	6079.223	Fe	6400.200	?
5791.207	Fe }	6102.408	Fe	6400.509	Fe
5798.087	?		Ca }	6408.231	Fe
5798.400	Fe	6102.941	Fe }	6411.864	Fe
5805.448	Ni	6103.449	?	6420.171	Fe
5806.954	Fe	6108.338	Ni	6421.569	Fe
5809.437	Fe	6111.287	Ni	6431.063	Fe
5816.594	Fe	6116.415	Fe	6439.298	Ca
5831.832	Ni	6122.428	Ca	6450.029	Ca
5853.903	Ba	6136.834	Fe	6462.835	Ca }
5857.672	Ca	6141.934	Fe-Ba		Fe }
5859.810	Fe	6154.431	Na	6471.881	Ca
5862.580	Fe	6160.970	Na	6480.264	atm. (H ₂ O)
[D ₂] 5875.982	He	6162.383	Ca	6482.099	?
	Fe	6169.260	Ca	6494.001	Ca
5884.048	at. (H ₂ O) }	6169.775	Ca	6495.209	Fe
5889.854	atm. (H ₂ O)	6173.554	Fe	6499.871	Ca
[D ₂] 5890.182	Na	6177.028	Ni	6516.315	?
5893.098	Ni	6180.419	Fe	6518.594	Fe
[D ₁] 5896.154	Na	6191.397	Ni	6532.546	atm. (H ₂ O)
	at. (H ₂ O) }	6191.770	Fe	6534.173	?
5898.395	Fe? }	6200.533	Fe		Ti }
	at. (H ₂ O) }	6213.646	Fe	6546.486	Fe }
5901.681	Fe? }	6219.493	Fe	6552.840	atm. (H ₂ O)
5905.895	Fe	6230.946	Fe-V	[C] 6563.054	H
5914.384	Fe }	6237.529	?	6569.461	Fe
	?-at. (H ₂ O) }	6246.530	Fe	6572.312	atm. (H ₂ O)
5916.475	Fe	6252.776	Fe	6574.477	?
5919.855	atm. (H ₂ O)	6254.454	Fe	6575.179	Fe

ROWLAND'S TABLE.—Continued.

6593.161	Fe	6889.194	atm. (O)	7148.427	?
6594.115	Fe	6890.149	atm. (O)	7168.191	?
6609.354	Fe	6892.614	atm. (O)	7176.347	at. (H ₂ O)?
6633.992	Fe	6893.559	atm. (O)	7184.781	at. (H ₂ O)?
6643.882	Ni	6896.292	atm. (O)	7186.552	at. (H ₂ O)?
6663.525	?	6897.195	atm. (O)	7193.921	atm. (H ₂ O)
6663.696	Fe	6900.199	atm. (O)	7200.753	atm. (H ₂ O)
6678.232	Fe	6901.113	atm. (O)	7201.468	atm. (H ₂ O)
6703.813	?	6904.358	atm. (O)	7216.812	at. (H ₂ O)?
6705.353	?	6905.263	atm. (O)	7223.930	?
6717.934	Ca	6908.785	atm. (O)	7227.765	?
6722.095	?	6909.675	atm. (O)	7232.509	?
6726.923	Fe	6913.454	atm. (O)	7233.171	?
6750.412	Fe	6914.328	atm. (O)	7240.972	atm. (H ₂ O)
6752.962	Fe	6914.819	Ni	7243.904	atm. (H ₂ O)
6768.044	Ni	6916.957	?	7247.461	at. (H ₂ O)?
6772.565	Ni	6918.363	atm. (O)	7264.851	at. (H ₂ O)?
6787.137	Fe	6919.245	atm. (O)	7265.833	at. (H ₂ O)?
6807.100	Fe	6923.557	atm. (O)	7270.205	?
6810.519	Fe	6924.420	atm. (O)	7273.256	at. (H ₂ O)?
6820.614	Fe	6928.992	atm. (O)	7287.689	at. (H ₂ O)?
6828.850	Fe	6929.838	atm. (O)	7290.714	at. (H ₂ O)?
6841.591	Fe	6934.646	atm. (O)	7300.056	atm. (H ₂ O)
6843.908	Fe	6935.530	atm. (O)	7304.475	at. (H ₂ O)?
6855.425	Fe	6947.781	at. (H ₂ O)?	7318.818	at. (H ₂ O)?
6867.461	atm. (O)		at. (H ₂ O)?	7321.056	?
6867.800	atm. (O)	6953.838	atm.?	7331.206	?
6868.124	atm. (O)	6956.700	atm. (H ₂ O)	7389.696	?
6868.393	atm. (O)	6959.708	at. (H ₂ O)?	7409.554	?
6868.779	atm. (O)	6961.518	at. (H ₂ O)?	7446.038	?
6869.141	atm. (O)	6978.655	?	7462.609	?
6869.347	atm. (O)	6986.832	atm. (H ₂ O)	7495.351	?
[B] 6870.186	atm. (O)	6989.240	at. (H ₂ O)?	7511.286	?
6871.179	atm. (O)	6999.174	at. (H ₂ O)?	7545.921	?
6871.527	atm. (O)	7000.143	?	7594.059	atm. (O)
6872.493	atm. (O)	7006.160	?	[A] { 7621.277	atm. (O)
6873.076	atm. (O)	7011.585	?	7623.526	atm. (O)
6874.039	atm. (O)	7016.279	at. (H ₂ O)?	7624.853	atm. (O)
6874.884	atm. (O)	7016.690	at. (H ₂ O)?	7627.232	atm. (O)
6875.826	atm. (O)	7023.225	?	7628.585	atm. (O)
6876.957	atm. (O)	7023.747	?	7659.658	atm. (O)
6877.878	atm. (O)	7024.988	?	7660.778	atm. (O)
6879.294	atm. (O)	7027.199	?	7665.265	atm. (O)
6880.176	atm. (O)	7027.726	?	7666.239	atm. (O)
6881.970	Cr	7035.159	?	7670.993	atm. (O)
6882.772	Cr	7038.470	?	7671.994	atm. (O)
6883.318	Cr	7040.058	?	7699.374	?
6884.083	atm. (O)	7090.645	?	7714.686	?
6886.008	atm. (O)	7122.491	?		
6886.987	atm. (O)	7147.942	?		

matter of accident is practically out of the question, as he¹ calculated that the chance of this being so is only 1 in a trillion ($\frac{1}{1000000000000000000}$). Actually the chance is even less, for it is found that, generally, the brighter an iron line the darker is the corresponding Fraunhofer line. In explanation of the above agreement he suggested that the light of the sun passes through the vapor of iron which absorbs certain of the rays. It is impossible to suppose that the earth's atmosphere contains sufficient iron to produce these absorption-lines, especially as they undergo no change when the sun approaches the horizon; the metal must therefore be present as vapor in the solar atmosphere, and since this must necessarily be at an enormously high temperature, the presence in it of vaporized iron is not inherently improbable. The occurrence of one terrestrial element in the solar atmosphere having been thus demonstrated, and a considerable number of the Fraunhofer lines accounted for, Kirchhoff sought for evidence of the existence of other elements, and found calcium, magnesium, sodium, chromium, barium, copper, zinc, and nickel. The presence of cobalt, which is always found with nickel and iron in meteorites, he was unable to demonstrate positively. The following additional metals, which he investigated, appeared to be invisible in the solar atmosphere: gold, silver, mercury, aluminium, tin, lead, antimony, arsenic, strontium, lithium. The researches of Ångström and Thalén,² separately and in conjunction, increased the number of solar elements, and led to the identification of about eight hundred Fraunhofer lines. The following table shows how many of the lines included in Ångström's spectrum tables originate from known elements.

¹ Untersuchungen über das Sonnenspectrum. A. B. A. 1861.

² Recherches sur la spectre solaire (Upsala, 1868).

Element.	Number of lines.	Element.	Number of lines.
Aluminium.....	2 ?	Iron	450
Barium.....	11	Magnesium.....	4 + (3?)
Calcium.....	75	Manganese.....	57
Chromium.....	18	Nickel	33
Cobalt	19	Sodium.....	9
Copper.....	7	Titanium.....	118
Hydrogen.....	4	Zinc.....	2 ?

This list was considerably increased by Lockyer,¹ and light thrown on doubtful points by his method of long and short lines. The appearance in the solar spectrum of some, but not all, the reversed coincident lines of certain elements had been noticed by Kirchhoff in the case of cobalt. Lockyer showed that the production of spectrum lines is dependent on the temperature, pressure, quantity, and purity of the vapor of the element. The longer lines require a lower temperature, and are most easily visible. The shorter lines cannot be expected to appear always in the relatively cool atmosphere surrounding the sun, consequently their absence does not necessarily prove that a particular element is not present in the sun, but the appearance of the long lines is sufficient to establish its existence. The same considerations explain why the long lines only are reversed; this is accomplished by the cool atmosphere which, on account of its temperature, can only affect these and not the short ones. In addition to the elements given above, Lockyer has found the following in the sun: lead, cadmium, potassium, cerium, strontium, uranium, vanadium, and probably also lithium, rubidium, cæsium, tin, bismuth, and silver. Lockyer has been led by his observations to certain other conclusions which have failed to meet with general acceptance. The relative intensity of the Fraunhofer lines sometimes varies; from a comparison of these with coincident spectrum lines he considers that some elements are dissociated in the sun; this gives rise to certain fundamental or "basic lines," due to a common constituent of several

¹ Studies in spectrum analysis (New York and London, 1878).

elements. The incorrectness of this view has been established by Liveing and Dewar,¹ Fiévez,² H. W. Vogel,³ Kayser and Runge,⁴ Rowland,⁵ and others. It has been shown that, with few exceptions, the intensity of the solar lines is almost the same as that of the arc spectra of elements, that Lockyer has confused groups of lines with single ones, and has mistaken the character of the lines. The basic lines have been resolved by the use of higher dispersions, so that their coincidence loses its significance; in the remaining cases the phenomena are due to the presence of a common impurity in the elements examined. The number of elements observed in the sun by Lockyer has also been modified. Kayser and Runge's work on the spectra of the elements included an investigation of their presence in the sun; they showed the absence of potassium, lithium, cæsium, and rubidium. The existence in it of carbon and nitrogen was proved by means of the bands, produced by a compound of these elements, and usually termed the cyanogen bands.

During the past few years Rowland⁶ has thoroughly examined the Fraunhofer lines, and with the help of the concave diffraction grating has also photographed the spectra of the elements in order to compare them with his solar atlas; the chief results of this work are given in the preceding table of wave-lengths. He finds that the following additional elements are present: lithium, scandium, yttrium, zirconium, beryllium, germanium, and erbium. The lists below reproduce his arrangement of elements known with certainty to be present in the sun; in the first they are arranged according to the intensity, in the second according to the number of the

¹ P. R. S. (1881) 32, 225.

² Ann. de l'observ. de Bruxelles (1882), [2] 11.

³ P. M. (1883), [5] 15, 28

⁴ A. B. A. 1890.

⁵ Johns Hopkins Univ. Circulars (1891), 10, 42.

⁶ *Ibid.* (1891), 10, 41.

lines. All elements except those marked † occur occasionally as bright lines in the chromosphere.

Intensity.	Number.	Intensity.	Number.
1. Calcium	Iron (at least 2000)	18. Yttrium.....	Palladium
2. Iron.....	Nickel	19. Zirconium†.....	Magnesium (at least 20)
3. Hydrogen	Titanium	20. Molybdenum†.....	Sodium (11)
4. Sodium.....	Manganese	21. Lanthanum.....	Silicon
5. Nickel.....	Chromium	22. Niobium†.....	Hydrogen
6. Manganese.....	Cobalt	23. Palladium†.....	Strontium
7. Cobalt.....	Carbon (at least 200)	24. Neodymium†.....	Barium
8. Silicon†.....	Vanadium	25. Copper†.....	Aluminium (4)
9. Aluminium†.....	Zirconium	26. Zinc.....	Cadmium
10. Titanium	Cerium	27. Cadmium.....	Rhodium
11. Chromium.....	Calcium (at least 75)	28. Cerium.....	Erbium
12. Strontium.....	Neodymium	29. Beryllium.....	Zinc
13. Manganese.....	Scandium	30. Germanium†.....	Copper (2)
14. Vanadium	Lanthanum	31. Rhodium†.....	Silver
15. Barium.....	Yttrium	32. Silver.....	Beryllium
16. Carbon†?.....	Niobium	33. Tin.....	Germanium
17. Scandium†.....	Molybdenum	34. Lead.....	Tin
		35. Erbium.....	Lead (1)
		36. Potassium†.....	Potassium

DOUBTFUL ELEMENTS.

Iridium	Platinum	Tantalum	Tungsten
Osmium	Ruthenium	Thorium	Uranium

ABSENT FROM THE SOLAR SPECTRUM.

Antimony	Cæsium	Nitrogen (as in a vacuum tube)	Selenium
Arsenic	Gold	Phosphorus	Sulphur
Bismuth	Indium	Praseodymium	Thallium
Boron	Mercury	Rubidium	Lithium

ELEMENTS NOT YET INVESTIGATED BY ROWLAND.

Bromine	Fluorine	Holmium	Oxygen	Terbium
Chlorine	Gallium	Iodine	Tellurium	Thulium, etc.

The above results, although obtained by the best methods, are by no means final. The number of Fraunhofer lines which has been identified is large, but there are numerous prominent ones the origin of which is unknown; many are possibly due to silicon, the lines of which in the visible

region are extremely difficult to obtain, although those in the ultra-violet can be readily observed. There are probably more iron lines in the solar spectrum than those at present recognized, and it is possible that, at more elevated temperatures than those hitherto attainable, the lines of all elements may increase in number. The investigation of many spectra has been far from thorough, and extended work in this direction will probably result in the identification of numerous Fraunhofer lines. The spectra of the metals of the rare earths has been much neglected; Rowland¹ examined several of them and found that cerium, lanthanum, praseodymium, and thorium cannot be further resolved. Yttrium probably consists of two substances, erbium certainly of three and possibly of four elements; one of these, termed by Rowland demonium on account of the difficulty of its separation, occurs in the sun, and exhibits a strong line at about $\lambda = 4000.6$. Rowland has also isolated four other elements designated by the letters *h*, *n*, *k*, *e*, three of them exhibit a feeble absorption-spectrum in the visible region, and a strong one in the ultra-violet.

Telluric Lines of the Solar Spectrum.—Reference has already been made to the *telluric* or *terrestrial* Fraunhofer lines produced by the atmosphere (comp. spectrum of air, Chapter VII). Rowland's table of wave-lengths shows that the oxygen and water vapor of the atmosphere are the only substances which produce absorption in the visible region; nitrogen, carbon dioxide, and ozone appear to exert no influence. Egoroff,² Janssen,³ Cornu,⁴ and Becker⁵ have investigated the behavior of oxygen, and Ångström⁶, and

¹ Johns Hopkins Univ. Circulars (1894) 13, 73.

² C. r. 93, 385, 788; 95, 447; 97, 555.

³ *Ibid.* 54, 1280; 56, 538; 60, 213; 63, 728. A. c. p. [4] 23, 274.

⁴ C. r. 98, 169. Journ. de Phys. [2] 3, 109. W. A. Beibl. 8, 305. A. c. p. [6] 7, 5.

⁵ T. R. S. E. (1890) 36, 1.

⁶ C. r. (1866) 63, 647. Recherches sur le spectre solaire (Upsala, 1868).

Janssen¹ that of water vapor. In addition to known terrestrial elements, the Fraunhofer lines have led to the identification of others which have either not yet been isolated at all, or have only been obtained long subsequent to their spectroscopic characterization. This applies to the D_3 -line, produced by the element which Frankland termed helium, and to the bright green line of the corona designated by Kirchhoff 1474K. As already stated, Ramsay² has recently obtained helium from clèveite.

Limits of the Investigation.—It is somewhat surprising that so many terrestrial elements, such as the non-metals, and the metals of high atomic weight, appear to be absent from the sun, but the investigation can only proceed a certain length. It has been already stated that, in the ultra-violet, the solar spectrum does not extend beyond about $300\mu\mu$. As the temperature rises spectra tend to develop in the violet; hence, on account of the extremely high temperature of the sun, a considerable portion of its spectrum must necessarily escape observation. Cornu³ states that the absorption of the ultra-violet region is not caused by the varying constituents of the atmosphere, such as water vapor or dust, but essentially by nitrogen and oxygen. He⁴ has suggested a formula for the calculation of the length of the solar spectrum absorbed by the column of air which the light traverses; according to this, a thickness of 663 metres causes a diminution of 10 \AA . at the ultra-violet end. The formula indicates that the extreme limit which can be observed is w.-l. = 2930, and it also shows that at w.-l. = 2120 and w.-l. = 1570 total absorption is caused by strata of air 10 m. and 0.1 m. in thickness, respectively. This was confirmed by experiment: the triple line of aluminium of w.-l. = 1860 was rendered unrecognizable by passage through a column of

¹ C. r. (1866) 63, 289, 728. A. c. p. (1871) [4] 23, 274; 24, 215.

² C. N. (1893) 71, 151.

³ C. r. 90 940

⁴ *Ibid.* 88, 1285; 89, 808.

air 4 m. in length. A further obstacle to the determination of the chemical composition of the sun is the fact that its nucleus, comprising at least nine tenths of the whole, is not available for spectroscopic investigation, as explained below.

The Physical Condition of the Sun.—In order to explain the occurrence of the dark lines in the solar spectrum Kirchhoff concluded that the atmosphere of the sun encloses a luminous mass which emits a continuous spectrum of high illuminating power. This inner portion is either solid or liquid, and at a higher temperature than the atmosphere. Subsequent investigations, both under ordinary conditions and during solar eclipses, have shown that the sun is more complex than Kirchhoff imagined. A complete treatment of the subject is altogether beyond the scope of this work, particularly as opinion is still much divided; the majority of investigators agree with C. A. Young's¹ views, and it will suffice to attempt a brief sketch of these.

The nature of the *inner nucleus* of the sun can only be conjectured, as it is beyond the reach of observation. Probably it consists of gas at an extremely high temperature, and under such an enormous pressure that its properties must resemble, to some extent, those of a viscous substance like putty. Surrounding the nucleus is the *photosphere*, composed of glowing cloud-like masses of vapor; it forms the visible surface, and appears to correspond with the clouds in the terrestrial atmosphere. It is not known whether it is separated from the nucleus by a definite surface; externally, it is sharply but irregularly defined, being elevated in some places into *faculæ*, and in others depressed, forming *spots*. The *reversing layer* is situated directly over the photosphere, and produces the Fraunhofer lines; its thickness is only about 1000 miles. The gases composing the reversing layer are not confined exclusively to the surface of the photosphere; they also occupy

¹ The Sun. New York and London, 1896.

the spaces between the photospheric clouds, and constitute the atmosphere in which these float. Above the reversing layer is the scarlet-red chromosphere, consisting of uncondensed gases (hydrogen and helium); from this numerous prominences extend far beyond the surface of the sun. The exterior portion of the sun is termed the corona; it consists of clouds and irregular streams of light, and gradually merges into the surrounding darkness. The greater portion of the mass of the sun is within the photosphere, but the larger part of its volume is outside it; the diameter of the solar atmosphere is at least double that of the central portion, and its volume consequently seven times as great as this.

The idea that the NUCLEUS of the sun consists of gas is supported by the fact that its atmosphere has a temperature sufficient to vaporize metals, and also because the sun's mean density is low. Compared with that of the earth it is only 0.253, or in comparison with water 1.406; it would necessarily be much greater than this if it consisted to a great extent of liquid iron, titanium, magnesium, etc. As the temperature of the gaseous mass is far above its critical point, the high pressure must cause it to exceed water in density, and therefore the gases must be viscous, and comparable in properties with molten glass or putty.

The PHOTOSPHERE is undoubtedly a gaseous envelope, condensed in places to cloudlike masses of vapor in consequence of the heat radiating into space. Its irregular appearance is due to these masses, the solid or liquid particles of which cause its luminosity, and produce a continuous spectrum like the solid particles in an ordinary flame. The spectrum of the SUN-SPOTS exhibits a number of dark bands; the dark lines of calcium, iron, titanium, etc., are widened, and some lines, like those of hydrogen, are often reversed; the sodium lines are also frequently enormously widened, and doubly reversed, as shown in Fig. 43. These phenomena render it likely that the increased absorption is due to gases

and vapors rushing in to fill a space, and absorbing the light emitted from the cavity. In consequence of the violent motion of the gases, lines are sometimes displaced, as explained in the following chapter.

The FACULÆ show the *H* and *K* bands of calcium, always reversed by a thin bright line running down the middle of each; and, whilst the reversal directly over a spot is generally

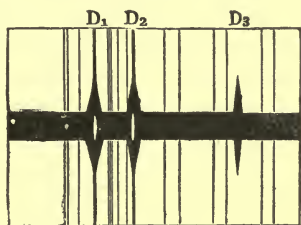


FIG. 43.

“single,” it is usually “double” in the faculous region surrounding it, i.e., the bright line is double. This makes it somewhat probable that the faculæ are not mere protrusions from the photosphere, but luminous masses of calcium vapor floating in the solar atmosphere, and possibly identical with the prominences themselves. The emission spectrum of the REVERSING LAYER can only be observed during a total eclipse; at the moment when the sun is completely obscured by the moon the lines of the whole spectrum are seen to flash out brightly luminous.

Like the other phenomena, the spectra of the CHROMOSPHERE and its PROMINENCES were formerly only visible during an eclipse; but in 1868 Janssen¹ and Lockyer² independently, and almost simultaneously, devised a method by which these portions of the sun could be observed daily in a clear atmosphere. Zöllner³ and Huggins⁴ have suggested similar methods of procedure. A spectroscope of high dispersive power is employed, and the slit opened widely; if not too large, the whole prominence is then visible. The prominences appear to bear a certain relationship to the sun-spots and faculæ; they are divided into two classes—quiescent,

¹ C. r. (1868) 68, 93.

² P. R. S. (1868) 17, 91, 104, 128.

³ P. A. (1869) 138, 32.

⁴ P. R. S. (1868), 17, 302.

cloudlike, or hydrogen and helium prominences, and eruptive or metallic ones. The former resemble terrestrial clouds in appearance; the latter are highly luminous, but the degree of luminosity and the shape change with extreme rapidity. Their spectra is very complicated, and, as shown by the displacement of the lines, they often attain a velocity exceeding 100 miles per second. The size of the prominences varies between wide limits; the mean thickness of the chromosphere is about 7500 to 9500 km. (5000 to 6000 miles), therefore no prominence can be less than 7000 to 9000 miles. Secchi observed 2767 prominences; of these 1964 attained a height of 29,000 km. (18,000 miles), and 751 exceeded 43,000 km. (28,000 miles). Young, in 1880, observed a prominence extending a distance of 562,400 km. (350,000 miles), the longest hitherto noticed. The following lines form the spectrum of the true chromosphere, and are always present:

1.	7065.50	He	7.	[g] 4340.66	H γ
2.	[C] 6563.05	H α	8.	4101.85	H δ
3.	[D ₃] 5875.98	He	9.	3970.20	He
4.	[1474 Å] 5316.87	Coronal line	10.	[H] 3968.56	Ca
5.	[F] 4861.50	H β	11.	[K] 3933.86	Ca
6.	[J] 4471.80	He			

There are numerous additional lines sometimes visible; their occurrence depends on the comparative violence of motion of the solar atmosphere. The principal ones are the following:

6678.2	He	[b ₃] 5169.16	Fe	4491.5	Mn
6431.1	Fe	[b ₄] 5167.57	Mg	4490.2	Mn
6141.93	Ba	5018.6	Fe	4469.5	Fe
[D ₁] 5896.2	Na	5015.7	He	4245.5	Fe
[D ₂] 5890.2	Na	4934.25	Ba	4236.1	Fe
5363	Fe?	4924.11	Fe	4233.8	Fe
5284.6	Ti?	4922.2	He	4226.9	Ca
5276.21	Cr?	4919.1	Fe?	4215.67	Sr
5234.7	Mn	4900.3	Ba	4077.88	Ca
5198.2	?	4584.1	Fe	4026.0	He
[b ₁] 5183.79	Mg	4501.44	Ti	3889.1	H
[b ₂] 5172.87	Mg				

The Corona.—The corona is visible only during a total eclipse, and much uncertainty prevails as to its nature. In 1869 Harkness, Pickering, and Young independently observed the coronal line 1474 *K.*, of wave-length 5316.87, to which reference has already been made. Of the element which produces this line nothing is at present known; that it is far less dense than hydrogen is probable from the fact that the line remains clear and sharp during the most violent movements of the prominences. It was long believed that this bright line was the only one present in the spectrum of the corona, but others, including those of hydrogen and calcium, have been subsequently observed, chiefly by Schuster,¹ who in 1882, in Egypt, was able to detect about thirty. In addition to the bright lines Pickering and Eastman in 1869 noticed a faint continuous spectrum, in which Janssen, and also Barker detected some of the stronger Fraunhofer lines, *D*, *b*, *G*. It is now generally admitted that the corona consists of an atmosphere extending 300,000 miles, and of extreme tenuity. The nature of the streamers is still uncertain; some regard them as a sort of permanent aurora, their position and direction being determined by the sun's magnetic field of force, as the terrestrial fields of force direct the beams of the aurora borealis. Schaeberle believes them to be due to light emitted and reflected from streams of matter ejected from the sun by forces acting, in general, along lines normal to the surface of the sun, and most active near the centre of each sun-spot zone. The attempts of Huggins² and others to photograph the corona in ordinary daylight have not been successful.

¹ Abney and Schuster, P. T. 1884.

² P. R. S. 34, 409; 39, 108. Astron. Nachr. 104, 113. W. A. Beibl. 9, 755.

CHAPTER X.

OTHER CELESTIAL BODIES.¹ AURORA BOREALIS. ZODIACAL LIGHT. LIGHTNING. DISPLACEMENT OF THE LINES.

Fixed Stars.—The physical condition of the fixed stars resembles that of the sun. Their continuous spectra, traversed by rectangular dark lines, shows that they consist of an incandescent mass surrounded by a glowing atmosphere. Fraunhofer, in 1817, observed that the dark lines differ in the spectra of various stars, and that they do not correspond with those in the solar spectrum; various stellar spectra were also correctly characterized by him. After the foundation of an accurate system of spectrum analysis Secchi and H. C. Vogel divided stellar spectra into groups, according to the degree of development of the stars. The arrangement is as follows:

Class I. Stars at such high temperatures that the metallic vapors in their atmospheres exhibit only a slight absorptive power (white stars). The spectra consist (*a*) of strong hydrogen lines and feeble metallic lines (Sirius, Vega, and the majority of white stars); (*b*) of single feeble metallic lines without the strong hydrogen lines (β , γ , δ , ϵ Orionis); (*c*) of bright hydrogen lines, and the bright *D*₂-line (α Lyræ, γ Cassiopeiæ).

Class II. Stars which resemble the sun, have an atmosphere containing metals, and exhibit a spectrum containing strong absorption-lines. The spectra show, (*a*) in addition to

¹ Comp. Scheiner, *Die Spectralanalyse der Gestirne* (Leipzig, 1890), where a detailed account is given of the subject, with references to the literature.

the hydrogen lines, numerous strong metallic lines, especially in the yellow and green (Capella, Arcturus, Aldebaran); (*b*) numerous bright lines together with dark ones, and a few faint bands (*T* Coronæ).

Class III. Stars at such a low temperature that the substances composing their atmospheres have combined to form chemical compounds which produce absorption-bands (red stars). The spectra exhibit, (*a*) in addition to dark lines, bands, dark and sharply defined towards the violet, whilst towards the red they become irregular (α Herculis, α Orionis, β Pegasi). Most of the lines are due to iron, but it is undetermined whether the bands consist of aggregates of fine lines, or of strong lines extended laterally; (*b*) dark, very broad bands, sharply bounded towards the red, and gradually disappearing towards the violet. This type only includes stars of small magnitude, which is unfortunate, as the spectra suggests the possibility of their atmospheres containing glowing carbon.

The Planets and Moon.—Since the planets and moon reflect sunlight, their spectra must be essentially that of the sun, modified by absorption-lines or bands produced by their own atmospheres: Spectroscopic observation shows that Mercury, Venus, and Mars have atmospheres similar in nature to that of the earth, and containing aqueous vapor. The same applies to Jupiter and Saturn, but their spectra exhibit an additional absorption-band; whether this is caused by differences in temperature and pressure or by the presence of a new gas is undetermined. The atmospheres of Uranus and Neptune also differ materially from that of the earth, and contain an additional constituent in large quantity.

The spectrum of the *moon* is in every way identical with that of the sun, showing that it has no atmosphere, or only one of extreme tenuity. The satellites of Jupiter exhibit the same spectra as that of the planet itself, and appear to have identical atmospheres.

Comets.—The first spectroscopic observation of a comet was made by Donati in 1864; he found that the spectrum consisted of three bright bands superposed on a continuous spectrum, and that, in part at least, the comet was self-luminous. Four years later Huggins stated that the bright bands were identical with those obtained by passing electric sparks through ethylene. Subsequent accurate measurements made by H. C. Vogel, and Hasselberg showed that this is not the case, although the comets undoubtedly contain carbon in considerable quantity. A spectrum very similar to that of a comet is obtained by passing a continuous electric discharge through a mixture of a hydrocarbon and carbon monoxide. The comet I of 1882 was observed by H. C. Vogel to contain sodium; this was confirmed by Dunér and Bredichin, whilst Copeland and J. G. Lohse noticed iron lines in comet II of 1882, which passed within a few thousand miles of the sun. Huggins, in 1881, observed that the continuous spectrum exhibits the Fraunhofer lines, proving that a portion at least of its light is reflected sunlight. Photometric and spectroscopic observations of a sudden outburst of light in the case of comet I of 1884 showed that a part of the continuous spectrum is due to the comet's own luminosity. Hasselberg has suggested that this is probably caused by electrical forces, and observations of other kinds have rendered it very probable that comets are the seats of electrical activity.

Meteors and Shooting Stars do not lend themselves to spectroscopic observation on account of the short period during which they are visible. They exhibit a continuous spectrum, caused by the incandescence of the solid constituents, but in addition to this only the sodium line has been observed with certainty. The meteorites which fall on to the earth can all be analyzed by the ordinary chemical methods, so that their spectroscopic investigation is not of much importance.

Nebulæ.—The spectroscopic investigation of the nebulæ

is of considerable interest in connection with the Kant-Laplace hypothesis of the origin of the solar system. Formerly they were classified as divisible nebulae, which could be resolved into clusters of stars, and indivisible or true nebulae; but the latter were regarded as being capable of resolution if sufficiently powerful telescopes were available. The first spectroscopic observations of nebulae were made by Huggins in 1864; he noticed the existence of bright lines, showing the presence of luminous gases. The faintness of the light renders the investigation a matter of difficulty; with medium instruments three or four lines only are usually visible. The wavelengths are about 5004, 4957, 4861, 4341. By means of photographic processes about forty additional lines may be detected. The presence of hydrogen is known with certainty, and that of helium is probable, but the origin of the majority of the lines is unknown. Many of the nebulae exhibit a faint continuous spectrum in addition to the bright lines; its maximum is in the green, instead of the yellow. Vogel states that it shows no sign of discontinuity, but Copeland and Huggins consider that it appears to be resolved into lines. If this view is correct, the nebulous clusters of stars are masses of glowing gas, and are to be regarded as stellar systems, the individuals of which are gaseous.

Aurora Borealis.—This phenomenon is the result of electric discharges in highly rarefied air, and has been a frequent subject of spectroscopic observation. The spectrum exhibits a number of very faint lines, together with a characteristic bright green one of wave-length = 5571, which has been termed the aurora line. Its origin is not known, but H. C. Vogel, Zöllner, and Hasselberg agree in regarding the remaining portion of the spectrum as a modification of that of air.

The spectrum of the ZODIACAL LIGHT is a reflected solar spectrum; the faintness of the light necessitates the use of a wide slit, so that the Fraunhofer lines are unrecognizable.

The spectrum of LIGHTNING has been examined by many,

including Kundt, John Herschel, Laborde, H. C. Vogel, Joule, Procter, Young, and Schuster. The majority have detected the line spectrum of nitrogen, frequently in combination with a continuous spectrum, and occasionally with a band-spectrum of unknown origin. Schuster states that this last bears a very close resemblance to the spectrum, at the cathode, of a vacuum tube containing oxygen mixed with a small proportion of carbon monoxide.

DISPLACEMENT OF THE LINES.

The spectroscope has rendered important help to astronomers in elucidating the relative velocity of bodies in the line of collimation. In the sections on sun-spots and prominences it was mentioned that their extremely rapid motion produced a displacement of the spectrum lines. The explanation of this phenomenon is obtained from Doppler's¹ principle, first propounded in 1841, according to which the color of the light received on to the retina, or the pitch of a note changes if the source of light or sound approaches or recedes from the observer at a speed not too small in comparison to that of light or sound respectively. If the source of light or sound approaches the observer more waves will be received in a given time than if it were stationary, whilst if it is receding the number of waves will be less. The color or wave-length of a ray from an object approaching will therefore be diverted towards the violet, but will approximate to the red if the object is receding. The alteration, to a stationary observer, according to whether the light approaches or recedes, is given by the expression $\lambda_1 = \lambda \left(1 \pm \frac{\alpha}{v} \right)$, where λ = the wave-length of the ray, λ_1 = that produced by the motion, v being the velocity of light, and α that of the luminous body. Fig.

¹ Ueber das farbige Licht der Doppelsterne und anderer Gestirne des Himmels. Abhandl. K. Böhmischen Ges. d. Wissensch. (1841-2) [5] 2, 465.

44 shows the displacement of the *F*-line in the spectrum of a sun-spot. Huggins, in 1864, first employed the displacement of the lines to determine the velocity of Sirius in the line of

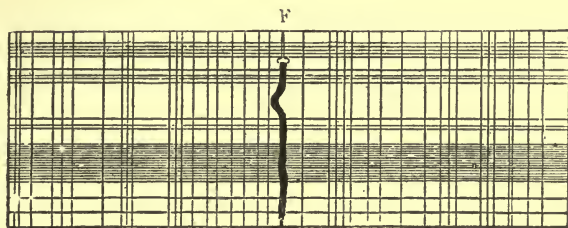


FIG. 44

collimation. He observed that the wave-length of the *F*-line had increased $0.109\mu\mu$; the velocity of light = 297,100 km. per second, and the wave-length of the *F*-line = $486.5\mu\mu$.

Consequently the expression $\frac{297100 \times 0.109}{486.5} = 66.6$ shows

that, at the time of the observation, Sirius and the earth were receding at the rate of 66.6 km. per second; but the earth was itself moving from Sirius at the rate of 19.3 km., so that the speed of the latter is reduced to 47.3 km. Subsequent observations, with improved instruments, led Huggins to modify this to 29—35 km. per second. Similar investigations of the stars and nebulae have been made by H. C. Vogel, Seabroke, and the Greenwich astronomers. Lockyer and Young have employed the method for the determination of the velocity of portions of the solar atmosphere, so far as they move in the line of collimation. The speed with which changes take place is enormous, and often resembles a violent cyclone; the rising and sinking masses of gas in the spots attain a velocity of 30 to 50 miles per second, whilst that of the prominences is frequently 150 km. (100 miles) per second, and occasionally twice as great.

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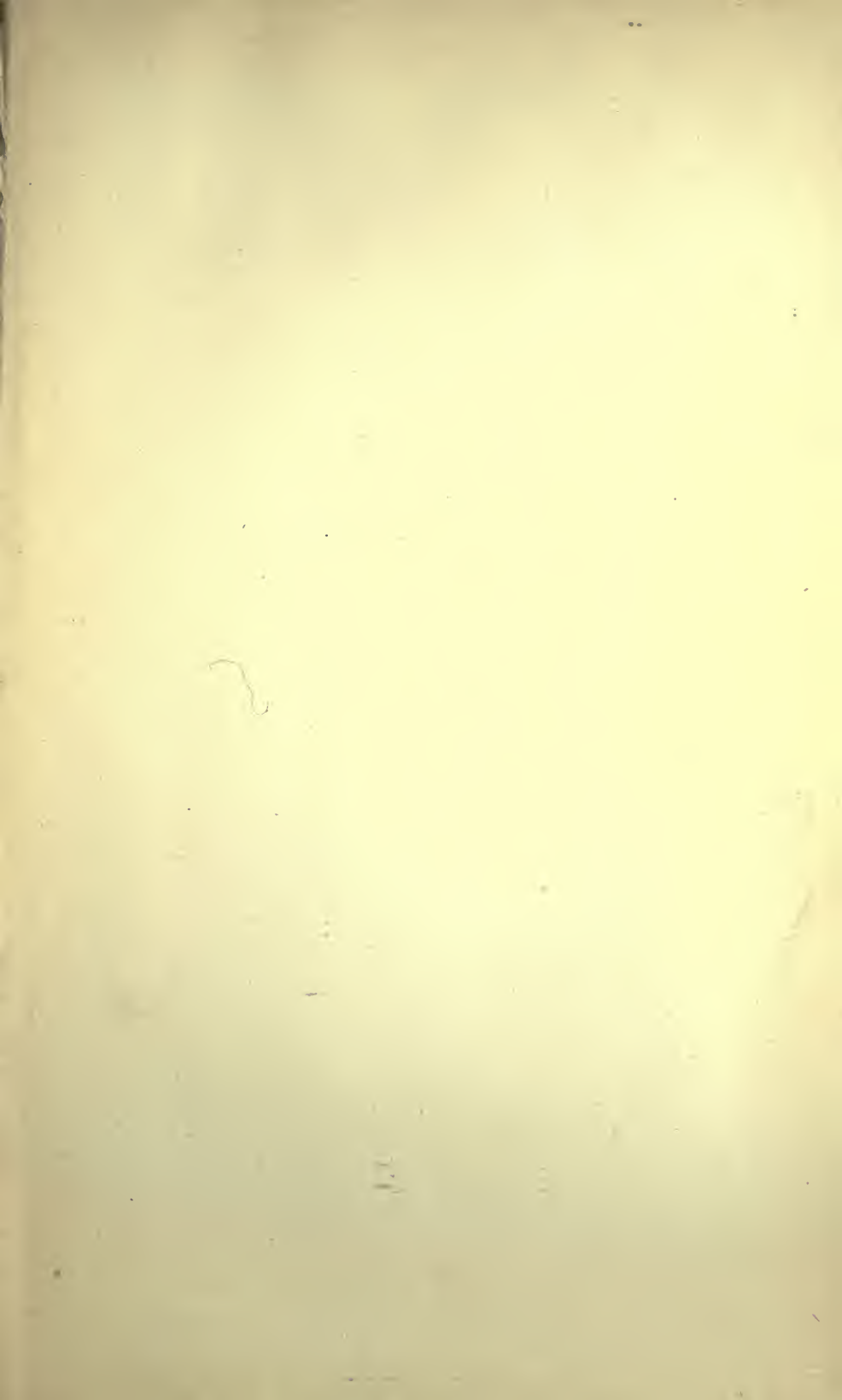
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